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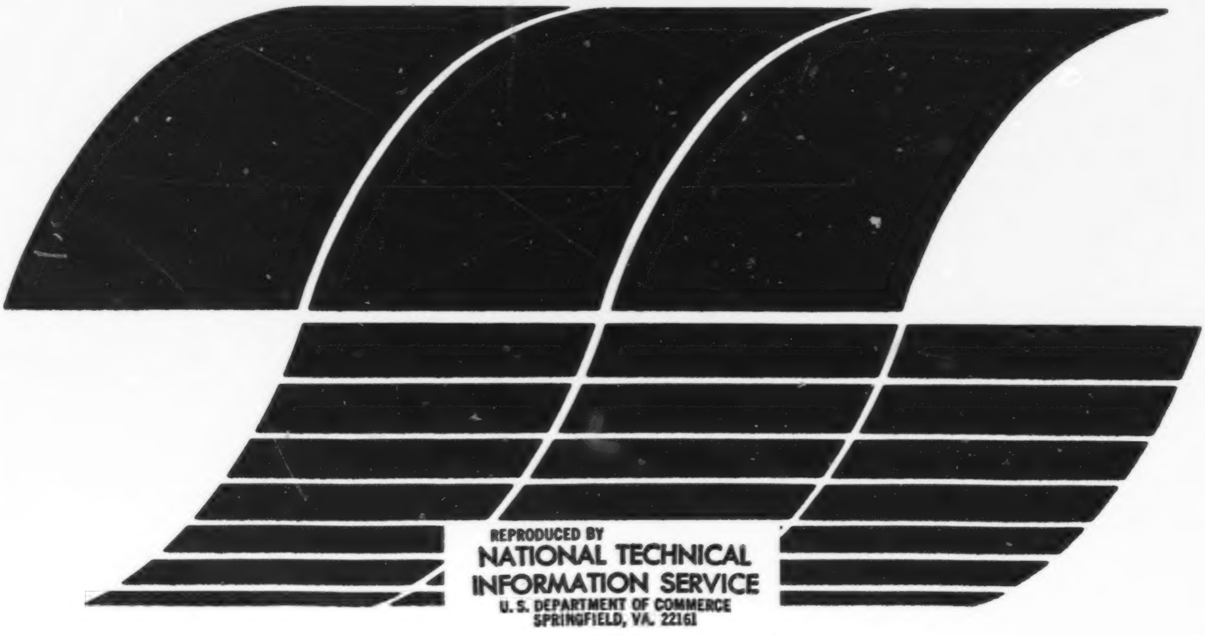

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Coal Gasification	Gases	Stationary Sources	13H
Desulfurization		Hot Gas Cleanup	07A,07D
Reduction (Chemistry)		Reducing Gases	07B,07C
Tars		Particulate	
Dust			11G
Nitrogen Oxides			

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ABSTRACT

Twenty-two hot gas cleanup (HGC) processes for desulfurizing reducing gases at temperatures above 430°C were identified and generically classified according to absorbent type into groups employing solid, molten salt, and molten metal absorbents. Each process is described in terms of its status, chemistry, operating characteristics, problems and uncertainties. The applicability of nine selected HGC processes to a variety of coal gasification systems is assessed for several end uses for the product gases. The advantages and disadvantages of HGC are evaluated relative to conventional low temperature cleanup systems with respect to thermal efficiency, the presence and/or emissions of tars, particulates and NO_x, and corrosion. Economic comparisons between HGC and low temperature desulfurization are also presented.

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SECTION I

INTRODUCTION AND SUMMARY

1.1 INTRODUCTION

Raw product gases from coal converters generally contain a variety of impurities which must be removed either because of process constraints or environmental regulations. Hydrogen sulfide, the major sulfur impurity in the raw product gas, can be removed by many commercially available technologies at temperatures below 150° C. However, for applications such as combined cycle electric power generation, cooling of the gas stream prior to combustion results in a reduced overall thermal efficiency. This energy inefficient step can be eliminated by removing hydrogen sulfide at elevated temperatures (e.g., above 430° C), namely by hot gas cleanup (HGC).

The general objectives of this study of hot gas cleaning processes, carried out under EPA Contract 68-02-2601, are to identify and determine the status of HGC processes in general, determine the applicability of these HGC processes to coal gasification systems, and compare the advantages and disadvantages of HGC generically with established low temperature cleanup processes.

1.2 SUMMARY

Section 2 of this report presents the conclusions derived from this study and the recommendations for further study. The status of HGC processes is described in detail in Section 3. The applicability of HGC processes to coal gasification systems is assessed in Section 4. Section 5 compares the relative merits of HGC with respect to low temperature desulfurization.

Literature and patent searches were conducted to identify HGC processes at all stages of development. The twenty-two identified HGC processes were then classified in Section 3 according to the following type of absorbents: solids, molten salts, and molten metals. The advantages and disadvantages of each generic type of absorbent were discussed. The solid absorbents were then classified according to the following types of active material employed in the sorbents: calcium, iron, copper, zinc and other ions. Information gathered on each HGC process was reviewed and employed to develop process descriptions and to describe process chemistry, research and development, and process status. Uncertainities and problems associated with each HGC process were also identified.

In Section 4, the applicability of HGC processes to various coal gasification systems is assessed. First, the type of gasification processes and the possible end uses were studied and matched. Then, the applicability of representative HGC processes to selected gasifier-end use pairs was evaluated. These evaluations were based on the thermodynamic equilibrium relationships for the hydrogen sulfide removal reactions, using the environmental regulations and process requirements as restrictions on the sulfur contents of the purified gases.

The advantages and disadvantages of HGC are assessed generically relative to low temperature cleanup systems in terms of thermal efficiency, the presence and/or emissions of tars, particulates, and NO_x, and corrosion. Economic comparisons between HGC and low temperature cleanup have previously been made by several investigators, and are summarized in Section 5.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

2.1 CONCLUSIONS

As a result of literature and patent searches, twenty-two HGC processes were identified. Table 1 summarizes these processes. Among them, only five are presently undergoing further development, with the others being terminated for various reasons. The IFP Process, one of the ongoing five processes, is being developed in France and is proprietary. Among these twenty-two HGC processes, only the Appleby-Frodingham Process has been employed on a commercial scale.

The following conclusions are drawn from this study:

- HGC processes are best suited for combined-cycle and on-site combustion applications coupled with low or intermediate Btu-gasifiers. The applicability of HGC processes for treating gases to be used as synthesis or reducing agents depends on the specific industrial process under consideration. The applicability of HGC processes for desulfurizing gases to be transported over long distances does not appear to be economically feasible.

- The applicability of nine HGC processes, each having a different active material in the absorbent, to nine gasification options and two end uses (namely, combined-cycle and on-site combustion) is presented in Table 17 of Section 4. Typical gasification characteristics, environmental regulations, process limitations, and theoretical thermodynamic relationships were considered in making the assessments that are summarized in Table 17. It can be seen from Table 17 that the Kennecott and MERC processes (or HGC processes using absorbents having Fe_2O_3 of Cu as active materials) are applicable for desulfurizing gases at high temperatures for any pair of the selected gasifier-end use pairs considered in this study.

- HGC processes provide greater overall thermal efficiencies than low temperature desulfurization. The difference in thermal efficiencies increases with increasing tar and steam contents in the raw product gas. In this respect, the Lurgi gasifier, coupled with combined cycle application seems especially attractive. For combined cycle applications which employ a gasification system producing tars and steam, HGC also provides a distinct advantage over low temperature desulfurization in terms of total capital requirements and cost of power. The difference in capital requirements and costs decreases for gasification systems producing gases which contain no tars and small amounts of steam.

TABLE 1- HGC PROCESSES

HGC PROCESSES EMPLOYING SOLID ABSORBENTS	STATUS	ABSORBENT	ABSORPTION TEMP. (°C)	PRESSURE (Pa)	GAS FLOW RATE (normal m^3/h)	METHOD OF REGENERATION	REGENERATION TEMPERATURE(°C)	COMMENTS
Calcium Based Absorbents								
Air Products	Terminated	MgO.CaO	649-871	1×10^5-2×10^5	79.3	H_2O-CO_2,Calcination	427-593;649-927	
Atlantic Refining-II	Terminated	$Ca(OH)_2$	316-538	7.0×10^5 - 4.8×10^6		NaOH solution-O_2	below solution b.p.t.	
CCNY	Terminated	Dolomite/ Fe_2O_3				H_2O-CO_2/Air	Panel Bed	No experimental work
CONOCO	Terminated	$MgO.CaCO_3$	900	1.5×10^6	17.7	H_2O-CO_2	593-760	
U.S. Steel	On-Going	MgO.CaO	Above 316	1×10^5	85.0	Proprietary		
Iron Based Absorbents								
Appleby-Frodingham	Terminated	Fe_2O_3	360-427	1×10^5	0.11×10^6	Air	593-816	Commercial
Babcock & Wilcox	Terminated	FeO	427-649		170	Air	538-649	
Battelle Columbus	Terminated	Supported Fe_2O_3	538-816	1×10^5	0.06	Air	593	
IMMR	On-Going	Gasifier Ash(Fe_2O_3)	371-816	4×10^5 - 9×10^5	1.22	Air	427-649	
MERC	On-Going	Supported Fe_2O_3	538-816	1×10^5-2×10^6	212	Air	538-816	Experimental work suspended
Copper Based Absorbents								
Atlantic Refining-I	Terminated	Cu/Pb/Zn alumino silicate	93-538			steam/air	371-538	
ESSO	Terminated	Supported Cu	299-982			Cu_2O	399-738	
John Hopkins	Terminated	Supported Cu/Cr/V	Up to 816			Air		Large Plant Tests
Kennecott	Terminated	Cu/CuO $Cu(OH)_2$	482-496	2×10^6 - 2.5×10^6		Air	816	

(continued)

TABLE 1 (cont'd)

HGC PROCESSES EMPLOYING	STATUS	ABSORBENT	ABSORPTION TEMP. (°C)	PRESSURE (Pa)	GAS FLOW RATE (normal m^3/h)	METHOD OF REGENERATION	REGENERATION TEMPERATURE(°C)	COMMENTS
Zinc Based Absorbents								
Catalysts & Chemicals	Terminated	ZnO	150-650	$6x10^5$ - $2.6x10^6$				Regeneration not studied
IFP	On-Going	Supported ZnO	400-600			O_2 Containing Gas	600-900	Proprietary Process
Other Solid Absorbents								
Exxon	Terminated	Supported La_2O_3	149-927	$1x10^5$ - $6x10^5$		Steam; Air/O_2		
Foster Wheeler	Terminated	Supported Ni	538-788		0.10	Air	538-788	
MOLTEN SALT ABSORBENTS								
Battelle Northwest	Terminated	Li, Na, K, Ca Carbonates	600-910	$1x10^5$	127	H_2O-CO_2	500-600	PDU Operated
HRI	Terminated	Supported K_2CO_3/ Na_2CO_3	907-1093	$1.2x10^6$ - $4x10^6$	0.01	H_2O-CO_2	907-1093	
Pullman	Terminated	Li, Na, K carbonates	816-1093	$1x10^5$ - $5x10^5$		Metal Bicarbonate-CO_2		
MOLTEN METAL ABSORBENTS								
IGT-Meissner	On-Going	Pb	327-1200			electrolysis	Above 327	Proprietary Process

- HGC processes add complications and uncertainities concerning the removal of particulates at high temperatures, whereas the removal of particulates at low temperatures can be considered as commercial technology.

- Processing of gases at high temperatures results in increased NO_x emissions from the downstream end use systems. In the case of low temperature desulfurization processes, most of the ammonia in the raw product gas is removed by water quenching.

- Another disadvantage introduced by HGC is the potential corrosion of metals by hydrogen sulfide at high temperatures.

2.2 RECOMMENDATIONS

Further research and development is recommended in the following areas:

- HGC Process R & D: None of the identified HGC processes presently appear to be ready for commercialization. The problems and uncertainties associated with HGC processes, as outlined in Section 3, need to be further studied. HGC processes employing molten salt or molten metal absorbents are complicated by serious corrosion and material handling problems. For this reason, future research and development should be focused on those processes employing solid absorbents. Among these HGC processes, those using iron and copper based absorbents are most likely to be applicable for a broad range of gasification systems.

- Particulates Removal: There is presently no commercial particulate removal equipment which could be operated at gasifier temperatures to reduce the particulate loadings in the fuel gas to levels required by environmental regulations and/or process restrictions for the end uses under consideration. Further research is needed in this area.

- NO_x Control: There is no available technology which can remove ammonia at high temperatures. However, the decomposition of ammonia into inert nitrogen and hydrogen might be a solution to the NO_x control problem. Research in this area should be emphasized.

- Corrosion: Research and development should be carried out to find suitable materials of construction to withstand corrosion by hydrogen sulfides and other chemical compounds such as alkali metal sulfides and chlorides.

SECTION 3

STATUS OF HGC PROCESSES

A comprehensive literature and patent search was carried out to identify HGC technologies at all stages of development. This search has been directed not only at HGC technologies developed specifically for coal conversion, but also for other related industrial applications such as coke-oven and refinery gases.

A computerized literature search was carried out at the Technical Information Center of Oak Ridge National Laboratory. The data base for this search includes Chemical Abstracts, Engineering Indices, U.S. and foreign patents and government publications. A thorough U.S. patent search was also conducted separately. HGC process developers and evaluators, HGC project officers at the U.S. Department of Energy, and other EPA contractors were contacted for additional information. Further references were obtained through the available publications.

Twenty two HGC processes were identified as a result of the information gathering efforts discussed above. These processes can be classified according to the type of absorbents, as follows:

- solid absorbents,
- molten salt absorbents, and
- molten metal absorbents.

Each absorbent reacts with the hydrogen sulfide present in the raw product gas to form sulfides, and thus purify the gas stream. The sulfided sorbents are usually regenerated by various means such as air, oxygen, steam, carbon dioxide, or a mixture of steam and carbon dioxide.

The status description presented herein contain comparisons of the advantages and disadvantages of the processes using the different generic types of absorbents, summarized process descriptions and related data, and detailed process descriptions, wherever possible.

3.1 HGC PROCESSES USING SOLID ABSORBENTS

The HGC processes using solid absorbents can be further classified according to the type of the active cation in the sorbent, as follows:

- calcium based absorbents,

- Iron based absorbents,
- copper based absorbents,
- zinc based absorbents, and
- other solid absorbents.

Both summarized and detailed information on these processes are given in the following sections.

The processes using solid absorbents generally have the advantage of incorporating process equipment and technologies (e.g., solids handling and disposal) employed on a commercial basis in a variety of industries. On the other hand, processes using molten absorbents can be considered to be more novel, and the operational difficulties associated with these processes seem to be more complicated than those using solid absorbents. For example, the corrosive nature of the melt often requires the use of special materials of construction whereas in the solid absorbent processes commercially available materials of construction are usually adequate. Other process difficulties encountered with molten absorbents, such as the solidification of the melt at cold spots in the system and the subsequent plugging of lines and equipment, do not occur in processes employing solid absorbents. Also, certain of the HGC processes using solid absorbents have been developed to a more advanced stage that those using molten salt absorbents. For example, the Appleby-Frodingham Process was used commercially for a number of years, and the Johns Hopkins Process was tested at commercial scale.

One of the most common problems associated with processes using solid absorbents is the loss of the physical strength of the absorbent. This was a major technical difficulty during the operation of the Appleby-Frodingham Process, which employed iron oxide absorbents. To minimize this problem, supported sorbents were developed. For example, in the MERC Process, which is a more recent process using iron oxide as active material, flyash or silica is incorporated as a support material to prevent the crumbling, carry over, and loss of sorbent material. Although supported sorbents reduce the amount of sorbent make-up and, therefore, the raw material costs, the preparation of such sorbents adds another process step and cost item.

A loss of activity was also observed for some processes at increasing numbers of absorption-regeneration cycles. Poor regenerability of the sulfided sorbent in the Air Products Process was one of the reasons for the termination of that process. For processes using oxygen or an oxygen containing gas for regeneration, temperature control in the regenerator bed can become a significant technical difficulty.

3.1.1 HGC Processes Using Calcium Based Absorbents

There are five HGC processes using calcium based solid absorbents. These processes are the Air Products, Atlantic Refining-II, CCNY, CONOCO and U.S. Steel Processes. All these processes have been terminated, with the exception of the U.S. Steel Process whose regeneration step is proprietary. A summary of information for these processes is presented below and in Table 2. Sections 3.1.1.1 through

TABLE 2 - HGC PROCESSES USING CALCIUM BASED SOLID ABSORBENTS

HGC PROCESSES	STATUS	ABSORBENT	ABSORPTION TEMP. (°C)	PRESSURE (Pa)	GAS FLOW RATE (normal) m^3/h	METHOD OF REGENERATION	REGENERATION TEMPERATURE (°C)	COMMENTS
Air Products	Terminated	MgO.CaO	649-871	1×10^5-2×10^5	79.3	H_2O-CO_2, Calcination	427-593 649-927	
Atlantic Refining -II	Terminated	$Ca(OH)_2$	316-538	7.0×10^5-4.8×10^6		NaOHsoln. O_2	below solution boiling point	
CCNY	Terminated	Dolomite/ Fe_2O_3				H_2O-CO_2/ Air	Panel Bed	No experimental work
CONOCO	Terminated	$MgO.CaCO_3$	900	1.5×10^6	17.7	H_2O-CO_2	593-760	
U.S. Steel	On-Going	MgO.CaO	Above 816	1×10^5	85.0	Proprietary		

3.1.1.5 contain detailed information on these processes.

- Air Products Process: The hydrogen sulfide from coal gases is removed with fully-calcined dolomite (MgO.CaO) at temperatures between 649 and 871°C (1200 and 1600°F). The sulfided sorbent is regenerated by first treating with steam and carbon dioxide at 427-593°C (800-1100°F) and then calcining at 649-927°C (1200-1700°F). Bench scale experiments were terminated in 1975 due to the poor regenerability of the sorbent, coke and tar deposition, and unfavorable process economics.

- Atlantic Refining Process - II : This process was developed to the bench scale level to remove hydrogen sulfide from the effluent gaseous streams of a hydrodesulfurization process or the first stage of a catalytic reforming process. In this process, an alkaline earth metal hydroxide, such as calcium hydroxide, is used as sorbent at temperatures from 316 to 538°C (600 to 1000°F) and pressures between 7.0 x 10^5 and 4.8 x 10^6 Pa (100 and 700 psi). The spent sorbent is regenerated by reacting it with an alkali metal hydroxide, such as NaOH, or sulfide in the presence of an oxygen containing gas. Research work was terminated in the mid 1950's.

- CCNY Process: A mathematical model was developed at the City College of New York to evaluate hydrogen sulfide removal using an absorbent, such as dolomite or iron oxide, in a panel bed filter, which was originally designed and tested for particulate removal from gases. Bench scale experiments were also carried out to study the rate of absorption of sulfur species with half and fully-calcined dolomite. However, the panel bed was never tested for sulfur removal, and there are presently no plans for further research in this area.

- CONOCO Process: Raw producer gas is desulfurized with half-calcined dolomite (MgO. $CaCO_3$) at about 900°C (1650°F) and elevated pressures (about 1.5 x 10^6 Pa; 15 atm). The spent dolomite is regenerated to calcium carbonate with carbon dioxide and steam at 700°C (1300°F). The regenerator outlet gas containing hydrogen sulfide is contacted with dilute hydrosulfurous acid to produce elemental sulfur at 154°C (310°F). Laboratory and continuous bench scale experiments were performed to test the process feasibility. Research work was terminated in 1977 due to lack of funding.

- U.S. Steel Process: Fully-calcined dolomite (CaO.MgO) is used to desulfurize coal gas at temperatures above 816°C (1500°F) and at atmospheric pressure. The regeneration method is proprietary. Work is ongoing at U.S. Steel at the pilot plant level.

3.1.1.1 Air Products Process: Air Products and Chemicals, Inc. developed and tested a process to desulfurize coal gases with fully-calcined limestone (1,2). The research program, which started in October 1972 and ended in January 1975, was funded by the Energy Research and Development Administration.

The Air Products Process contains three major process steps:

1. Calcination, at temperatures between 649 and 927°C (1200 and 1700°F)

$$CaCO_3 = CaO + CO_2 \quad \text{(endothermic).}$$

2. Absorption, at temperatures between 649 and 871°C (1200 and 1600°F)

$$CaO + H_2S = CaS + H_2O \text{ (exothermic)}.$$

3. Regeneration, at temperatures between 427 and 593°C (800 and 1100°F)

$$CaS + CO_2 + H_2O = CaCO_3 + H_2S \text{ (exothermic)}.$$

The calcination temperature depends solely on the carbon dioxide partial pressure. The equilibrium relationship for the CaO - $CaCO_3$ - CO_2 system is shown in Figure 1. A high calcination temperature is required when the carbon dioxide partial pressure is high.

The amount of H_2S removed from the producer gas depends on the feed gas H_2S, CO_2 and H_2O contents and the absorption temperature and pressure. The absorption temperature should be kept above the $CaCO_3$ calcination temperature (a function of the CO_2 partial pressure) to prevent the formation of $CaCO_3$. Figure 2 shows the dependency of the equilibrium constant on temperature for the reaction between CaO and H_2S. Lower absorption temperatures enhance increased H_2S removal efficiencies. The H_2S removal is adversely affected by the presence of steam in the inlet gas stream, although it is not influenced by a change in the pressure.

Regeneration of the sulfided sorbent is achieved with steam and carbon dioxide. The regeneration product is $CaCO_3$, which is then calcined to obtain CaO for use in another absorption cycle. The variation of the equilibrium constant with temperature for the reaction between CaS, CO_2 and H_2O is included in Figure 2. The regeneration reaction is favored by low temperature, high pressure, and high CO_2 and H_2O concentrations in the regeneration gas. These absorption and regeneration reactions were previously studied by Squires, et al. (3,4).

Initial bench-scale experiments were performed in a 100 cc fixed-bed quartz reactor at 1 atm. total pressure. No difficulty was observed during calcination of limestones. Absorption tests were performed by passing a tar-free and particulate-free hot synthetic producer gas (containing 0.6 percent H_2S) through the bed. High calcium (98 percent $CaCO_3$), magnesian (83 percent $CaCO_3$), siliceous (64 percent $CaCO_3$), and dolomitic (54 percent $CaCO_3$) limestones were found to be active for absorption of H_2S; however, no limestone appeared to be clearly superior to the others. Up to 75 percent calcium utilization was observed at 10 percent breakthrough (the point at which the exit H_2S concentration is 10 percent of the inlet gas H_2S concentration). Typical operating conditions were 816°C (1500°F), 1×10^5 Pa (1 atm) pressure, and a gas flow rate of 6,000 normal m^3/h per cubic meter (6000 SCFH per cubic foot) of limestone. The 10 percent breathrough point was observed after three or four hours of continuous on-stream absorption.

Regeneration was first attempted at low temperatures (66-93°C or 150-200°F), in aqueous phase, with water and carbon dioxide. However, these experiments were abandoned due to the pressure drop build-up resulting from bed agglomeration. Attention was then directed to vapor phase regeneration, varying the temperatures between 149 and 621°C (300 and 1150°F), since higher temperatures favor high reaction

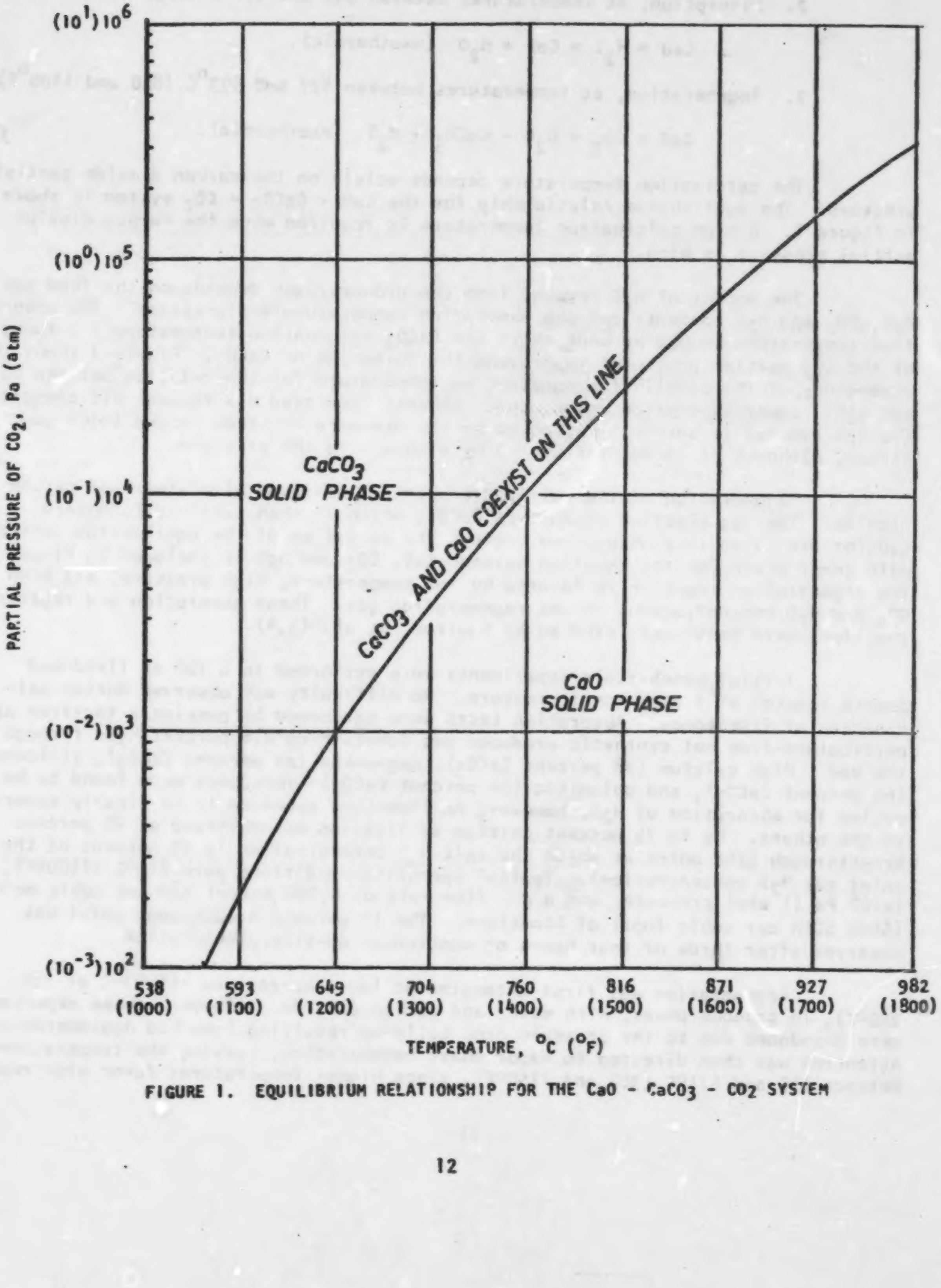


FIGURE 1. EQUILIBRIUM RELATIONSHIP FOR THE CaO - $CaCO_3$ - CO_2 SYSTEM

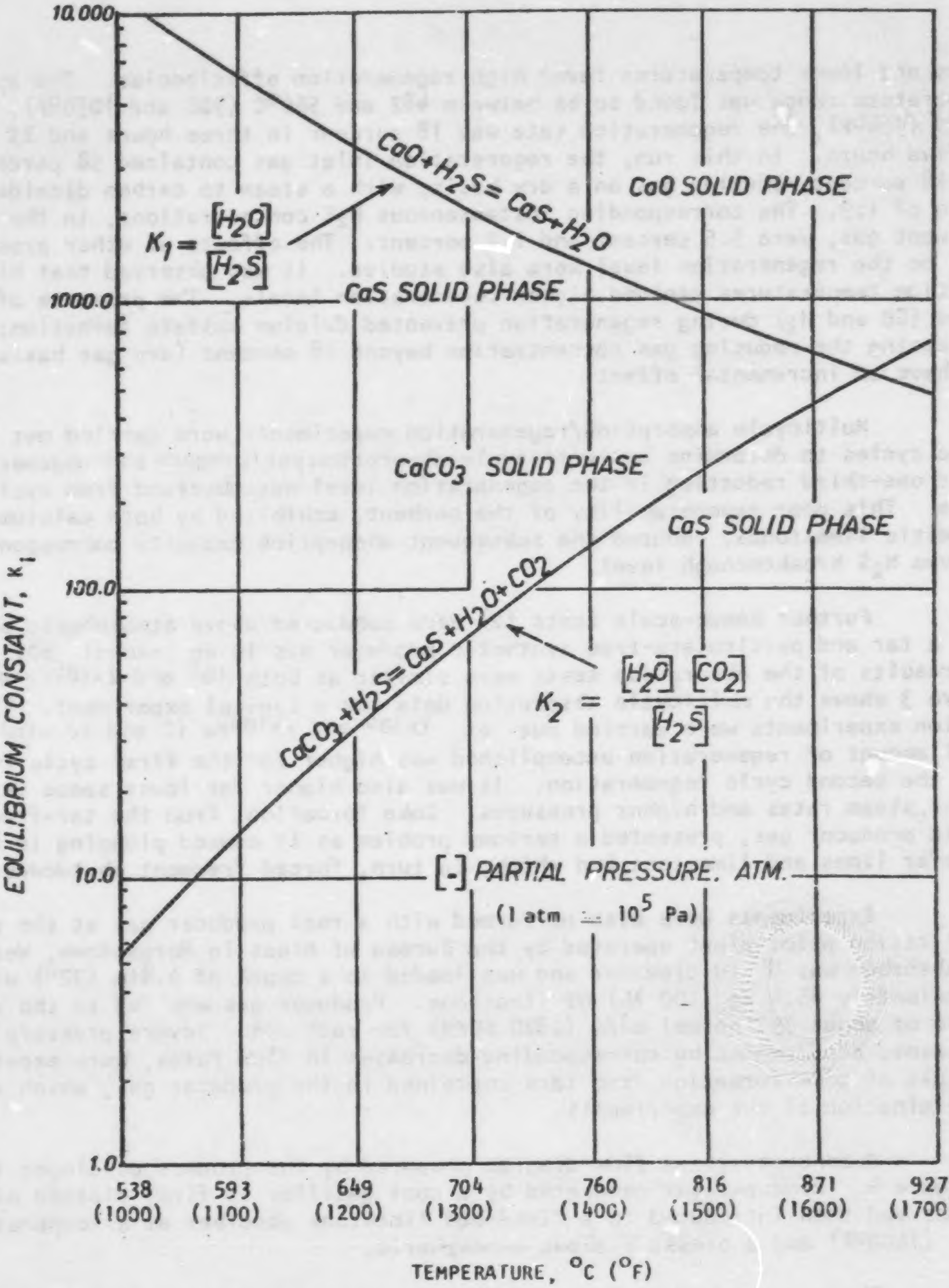


FIGURE 2. EQUILIBRIUM CONSTANTS FOR H_2S REACTING WITH CaO and $CaCO_3$

rates and lower temperatures favor high regeneration efficiencies. The optimum temperature range was found to be between 482 and 566°C (900 and 1050°F). At 518°C (964°F), the regeneration rate was 18 percent in three hours and 23 percent in five hours. In this run, the regeneration inlet gas contained 58 percent CO_2 and 18 percent reducing gas on a dry basis, with a steam to carbon dioxide mole ratio of 1:9. The corresponding instantaneous H_2S concentrations, in the dry effluent gas, were 5.5 percent and 1.2 percent. The effects of other process variables on the regeneration level were also studied. It was observed that higher calcination temperatures yielded higher regeneration levels. The presence of reducing gases (CO and H_2) during regeneration prevented calcium sulfate formation; however, increasing the reducing gas concentration beyond 18 percent (dry gas basis) did not have an incremental effect.

Multicycle absorption/regeneration experiments were carried out up to three cycles to determine cycle-to-cycle absorption performance and regenerability. About one-third reduction in the regeneration level was observed from cycle to cycle. This poor regenerability of the sorbent, exhibited by both calcium and dolomitic limestones, reduced the subsequent absorption capacity corresponding to a given H_2S breakthrough level.

Further bench-scale tests (2) were conducted above atmospheric pressure with a tar and particulate-free synthetic producer gas in an Inconel 601 reactor. The results of the absorption tests were similar at both 10^5 and $2x10^5$Pa pressures. Figure 3 shows the multicycle absorption data for a typical experiment. The regeneration experiments were carried out at $2x10^5$ and $1x10^6$Pa (2 and 10 atm). The total amount of regeneration accomplished was higher for the first cycle regeneration than the second cycle regeneration. It was also higher for lower space velocities, higher steam rates and higher pressures. Coke formation, from the tar-free synthetic producer gas, presented a serious problem as it caused plugging in the transfer lines and limestone bed which, in turn, forced frequent shutdowns.

Experiments were also performed with a real producer gas at the coal gasification pilot plant operated by the Bureau of Mines in Morgantown, West Virginia. The absorber was 8" in diameter and was loaded to a depth of 0.81m (32") with approximately 45.4 kg (100 lb) of limestone. Producer gas was fed to the reactor at a rate of about 793 normal m^3/h (2800 SCFH) for each run. Severe pressure drop increases, accompanied by corresponding decreases in flow rates, were experienced as a result of coke formation from tars contained in the producer gas, which resulted in termination of the experiments.

A conceptualized flow diagram prepared by the process developer is shown in Figure 4. Producer gas generated by a coal gasifier is first cleaned of particulates and then introduced to a fixed-bed limestone absorber at a temperature of 871°C (1600°F) and a pressure about atmospheric.

There are two absorbers operating in series, with the second functioning as a guardcase. At 10 percent breakthrough, the first absorber is taken off stream and cooled for regeneration, with the second absorber becoming the primary absorption vessel. The freshly regenerated absorber then becomes the second vessel. The purified gas is combusted in a power plant to produce steam for electric power generation.

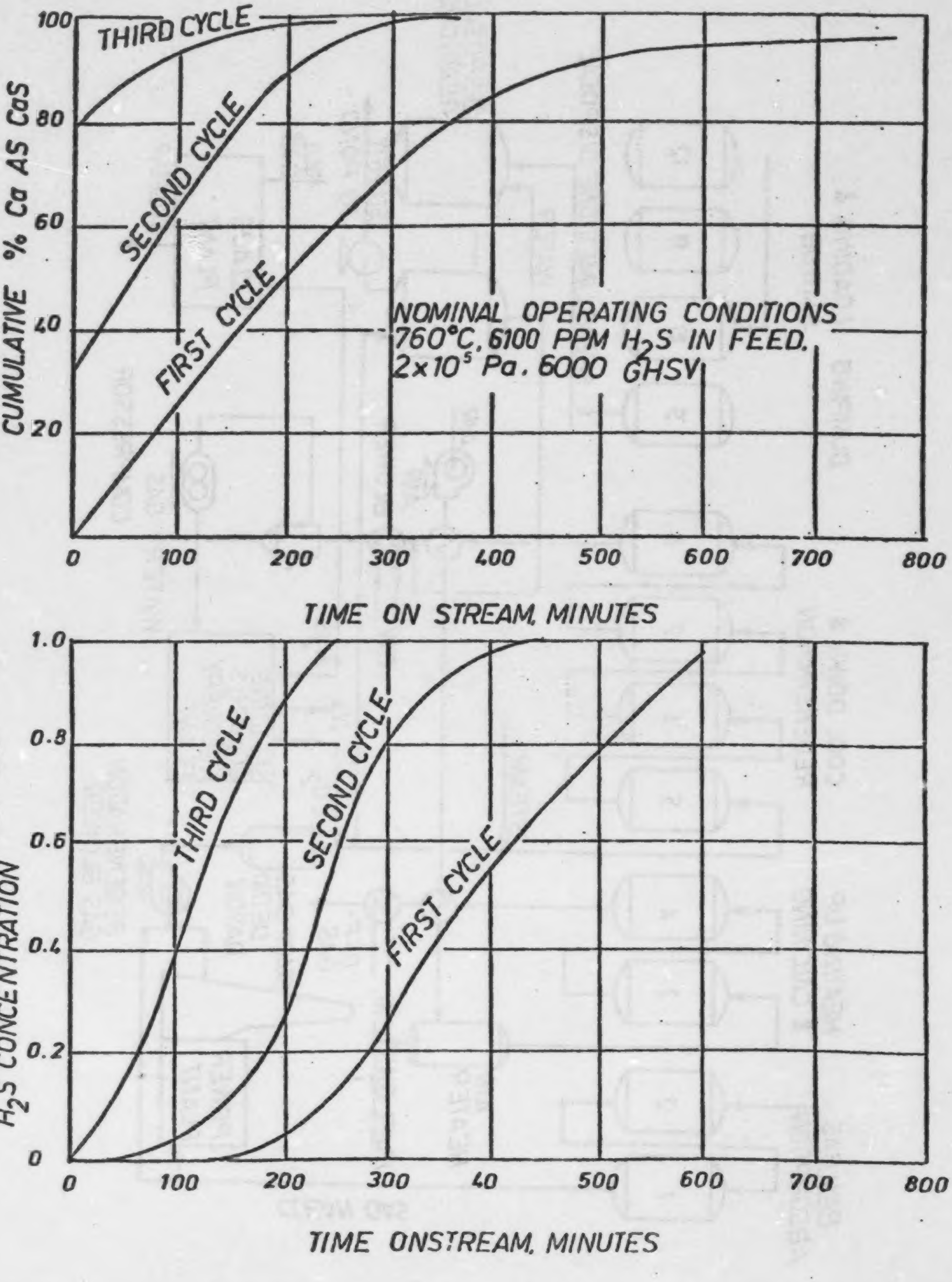


FIGURE 3. MULTICYCLE ABSORPTION DATA

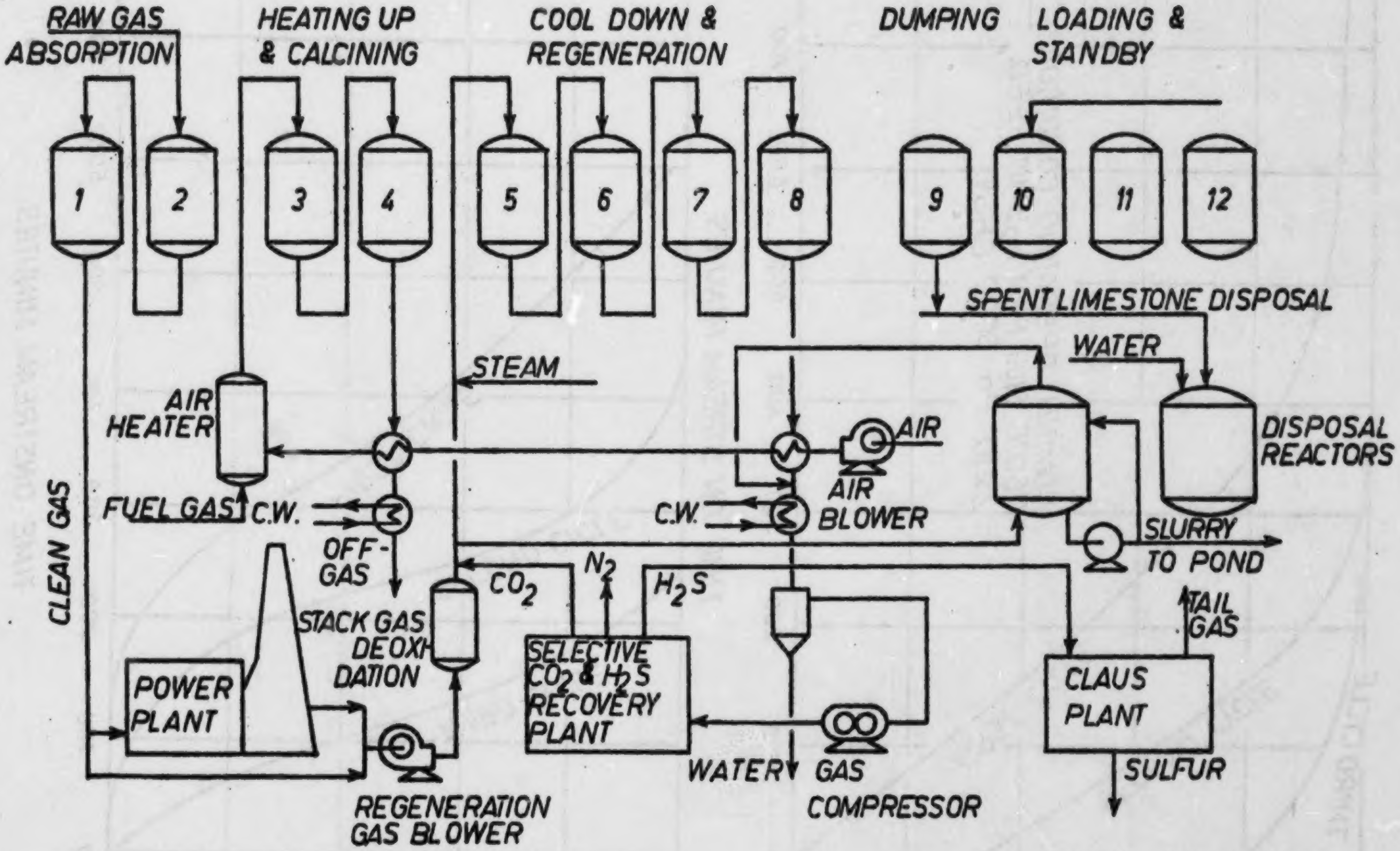

RAW GAS
ABSORPTION
HEATING UP
& CALCINING
COOL DOWN &
REGENERATION
DUMPING
LOADING &
STANDBY
1
2
3
4
5
6
7
8
9
10
11
12
SPENT LIMESTONE DISPOSAL
WATER
STEAM
AIR
HEATER
AIR
AIR
BLOWER
DISPOSAL
REACTORS
FUEL GAS
C.W.
C.W.
OFF-
GAS
CLEAN GAS
SLURRY
TO POND
CO2
N2
H2S
TAIL
GAS
STACK GAS
DEOXI
DATION
SELECTIVE
CO2 & H2S
RECOVERY
PLANT
POWER
PLANT
CLAUS
PLANT
SULFUR
WATER
GAS
COMPRESSOR
REGENERATION
GAS BLOWER

FIGURE 4. FLOW DIAGRAM OF THE AIR PRODUCTS PROCESS

The fully-sulifded bed of absorbent is cooled to 566°C (1050°F) at a pressure of approximately 4.8×10^5 Pa (70 psia) and regenerated; the regeneration gas is used for cooling. Four vessels in series are used for simultaneous cooling and regeneration. Because the H_2S concentration in the regeneration off-gas is too low (about 1.8 percent on a wet basis and 4.8 percent on a dry basis), it cannot be processed directly in a Claus plant. For this reason, after cooling and removal of water, this gas is compressed to a pressure of 1×10^6 to 2×10^6 Pa (150 to 300 psia) and directed to the selective CO_2 and H_2S recovery section. The H_2S rich stream from this section is sent to a Claus plant, while the CO_2 rich stream is added to the power plant stack gas and used for regenerating the sulfided limestone. The heat for calcination is provided from the combustion of clean fuel gas with air, with the calcined limestone being employed for absorption. The useful life of the limestone is ended after five absorption and four regeneration cycles. The sulfided limestone is then soaked with water and treated with CO_2 enriched-gas at 100°C (212°F) according to the Chance reaction:

$$CaS_{(s)} + CO_{2(g)} + H_2O_{(\ell)} = CaCO_{3(s)} + H_2S_{(g)}.$$

The limestone slurry is pumped to a settling pond and the H_2S containing gas is directed to the selective CO_2 and H_2S recovery unit.

An economic analysis of the process performed by the process developer is presented below. The size of the desulfurization process is based on an 800 MW power plant requiring 1.3×10^6 normal m^3/h ($4.5.5 \times 10^6$ SCFH) of producer gas $4.8 \times 10^6 J/normal\ m^3$, i.e. (130 Btu/SCF; or 2.65×10^5 kg/h , i.e., 292 tons/h , of coal at $2.88 \times 10^7 J/kg$, i.e. 12,400 Btu/lb).

Process Economics (Excluding Power Plant and Coal Gasifier)

Capital Cost	60 $/kw
Operating Expense	0.88¢/kg of coal
or	0.038¢/MJ
Energy Requirement	20 percent of the coal fired

The research program was terminated in January 1975 due to the poor regenerability of the limestone and coke and tar deposition, resulting in unfavorable process economics.

- Uncertainties and Problems: Poor regenerability of the sulfided limestone was one of the major problems encountered during the development of the Air Products Process. About one-third reduction in the regeneration level from one cycle to the next resulted in reduced calcium utilization in the absorption column. Experimentally, the best three-cycle calcium utilization averaged only 37 percent. However, in an economic analysis performed by the process developer, an "optimistic" average of 40 percent calcium utilization is assumed for five cycles.

Coke formation and deposition in the limestone bed were observed while operating with both synthetic and actual producer gas. With the actual producer gas, coking was caused by tars and heavy hydrocarbons. In addition, coke could arise from carbon monoxide according to the following reaction:

$$2\ CO = C + CO_2$$

(This reaction, however, is reversed at high temperatures and lower pressures.) In the experiments, coke formation caused plugging of the bed, which resulted in high pressure drops and equipment shut-downs. This problem could not be prevented during the process study. The process developer indicates that an oxidative process is an effective way to remove the coke. However, this method is damaging to the sulfided limestone since it generates sulfates that form low melting eutecitics with oxides and carbonates, causing sintering, loss of porosity, and loss of activity.

Corrosion of some metallic parts of the equipment was also observed during the experimental program. The reactor inlet line corroded at the point where cold and pure H_2S bottled gas mixed turbulently with the hot gases. Also, the inlet gas distribution plate of the reactor was plugged in a few instances, causing the cancellation of two experiments. An analysis of the residue of the plugging substance revealed that it was comprised chiefly of iron and nickel sulfides, originating from the corrosion. Since iron and nickel are more susceptible to H_2S attack than chrominum, the inlet lines and the gas distribution plate were changed from Inconel 601 to SS 316. The process developer indicates that materials of construction which can adequately withstand the corrosive atmosphere and conditions in producer gas desulfurization have not been developed, and may require the use of exotic alloys.

The Air Products Process consumes a large amount of energy. The process developer estimates that the total energy input to the system is equal to 9.5 percent of the clean producer gas heating value. This input is provided by electricity, natural gas and steam.

Finally, the Air Product Process generates a large quantity of solids for disposal. The process developer estimates that about 10 kg of limestone must be discarded for every 100 kg of coal gasified.

3.1.1.2 Atlantic Refining Process -II : The Atlantic Refining Process -II invented by Leum, et al. (5), removes hydrogen sulfide from high temperature/high pressure gaseous streams, either directly from a hydrodesulfurization process, or in the first stage of a catalytic reforming process. In the case of the hydrodesulfurization effluent, when the desulfurized stream is cooled to condense the liquefiable constituents, a liquid phase (free of dissolved hydrogen sulfide) and a gaseous phase (consisting of hydrogen sulfide-free effluent) would be produced. Alternatively, the hydrogen sulfide-free effluent could be sent to further refining operations, such as reforming or hydrocracking, without reducing either the temperature or presure of the effluent stream. In the case of a multiple stage catalytic reforming process, such as one utilizing a platinum-containing catalyst, a hydrocarbon-hydrogen stream, free of hydrogen sulfide, can be produced without deviating from the process conditions. Hot gas desulfurization provides savings in terms of energy and equipment costs.

The hydrogen sulfide containing gases are passed through a bed of alkaline earth metal hydroxide, such as calcium hydroxide, at temperatures between 316° and 538°C and pressures between 7.0×10^5 and 4.8×10^5 Pa (100 and 700 psi). The hydrogen sulfide reacts with the alkaline earth metal hydroxide to produce the corresponding alkaline earth metal sulfide and steam. If calcium hydroxide is used as a sorbent, then the following reaction takes place:

$$Ca(OH)_2 + H_2S = CaS + 2H_2O$$

When the sorbent is saturated, the gaseous stream from the hydrodesulfurization or catalytic reforming step is diverted to a second reactor containing a bed of fresh alkaline earth metal hydroxide. The first bed of alkaline earth metal sulfide is then regenerated in-place.

Regeneration is accomplished by treating the alkaline earth metal sulfide (e.g., CaS) with an alkali metal hydroxide (e.g., NaOH, KOH) or sulfide (e.g., Na_2S, K_2S) in an aqueous solution, at concentrations varying between 1 percent and 20 percent, while at the same time introducing an oxygen containing gas into the solution. The reaction produces the alkali earth metal hydroxide and alkali metal sulfide which, in the presence of oxygen, converts to water soluble alkali metal polysulfides. Based on the information given by Leum et al. (5), it is deduced that the following regeneration reactions can take place. It is assumed that the alkali metal is sodium and alkaline earth metal is calcium.

a) Regeneration with NaOH:

$$4\ CaS + 2NaOH + 3\ H_2O + \frac{3}{2}\ O_2 \longrightarrow 4\ Ca(OH)_2 + Na_2S_4$$

$$5\ CaS + 2NaOH + 4\ H_2O + 2\ O_2 \longrightarrow 5\ Ca(OH)_2 + Na_2S_5$$

b) Regeneration with Na_2S:

$$3\ CaS + Na_2S + 3\ H_2O + \frac{3}{2}\ O_2 \longrightarrow 3\ Ca(OH)_2 + Na_2S4$$

$$4\ CaS + Na_2S + 4\ H_2O + 2\ O_2 \longrightarrow 4\ Ca(OH)_2 + Na_2S_5$$

Regeneration can be carried out at any pressure below the boiling point of the aqueous solution. However, regeneration at the absorption pressure eliminates the need for depressuring and represurring the chamber containing the alkaline earth metal compound. The reaction time is between 4 and 12 hours with/air, at rates between 10 and 300 standard liters per mole of alkali metal hydroxide. The insoluble alkaline earth metal hydroxide pellets are separated from the solution and heated to desulfurization temperature with high temperature steam or inert gas, before the next absorption cycle is initiated.

A gas stream containing hydrocarbons, hydrogen and a small amount of hydrogen sulfide was passed through a bed of calcium hydroxide cylindrical pellets of 48mm (3/16") diameter and 32mm (1/8") thickness at 482°C (900°F) until the calcium hydroxide was completely converted to sulfide. Regeneration was achieved by passing air through calcium sulfide pellets in sodium hydroxide solutions for an hour. The amounts of sulfur removed in the regeneration were 34 percent, 66 percent, and 85 percent with 1 percent, 10 percent, and 20 percent sodium hydroxide solutions, respectively. With 14 percent Na_2S solution, only 55 percent of the sulfur was removed from the sulfided sorbent in two hours.

Further experiments were carried out to study successive desulfurization and regeneration cycles. Absorption was carried out at 482°C (900°F) by passing a gas containing hydrogen sulfide through a bed of calcium hydroxide pellets. Following the absorption period, the resulting pellets of calcium sulfide were treated with a 1 percent aqueous solution of sodium hydroxide at a temperature of 93°C (200°F) and atmospheric pressure. Air was used as the oxidizing agent. Absorption and regeneration efficiencies were maintained without loss during three cycles. The regeneration efficiency was found to be independent of the polysulfide concentration.

The Atlantic Refining Process – II was terminated in the late 1950's, and there are presently no plans for further process development. (A-1)

- **Uncertainties and Problems:** The limited available information on this process was obtained from a patent (5), in which the experimental difficulties are not mentioned.

Regeneration of the sulfided sorbent with an alkaline earth metal hydroxide and an oxygen containing gas produces polysulfides. The concentration of polysulfides increases with successive regeneration cycles. Although it was observed that regeneration efficiency is independent of polysulfide concentration, no method was proposed for the treatment of polysulfides to either recover sulfur or to dispose of it in an environmentally acceptable manner.

3.1.1.3 CCNY Process: City College of New York developed a panel bed filter to remove dust particles from a gas stream. The same device can, in principle, also be employed to remove hydrogen sulfide from coal gases at elevated temperatures, if a proper absorbent is used as the bed material. The panel bed filter has been tested experimentally only for particulate removal. However, a mathematical model was developed to study hot gas desulfurization in the panel bed filter.

Figure 17 illustrates the panel bed filter (6) which contains three columns of louvers. At the left of Figure 5 "wishbone louvers" support gas-entry surfaces of fine granular solid having sizes smaller than 20 mesh and larger than 100 mesh. This solid is supplied by gravity from an overhead bin to a tall, narrow space between the wishbone louvers and the central column of the closely spaced horizontal louvers. A coarse solid is held in place within a second tall, narrow space, between the central louvers and the inclined louvers at the right of Figure 5. When the panel bed filter is used for particulate removal, the dirty gas flowing in the horizontal direction enters the bed through the spaces between the adjacent wishbone louvers, and deposits a layer of dust at the entry surfaces. The clean gas leaves the other side of the panel bed filter (see Figure 6 a). The dust from the panel bed filter is removed by a reverse surge flow of a clean gas (puffback. A sharp puff of gas supplied to the clean face of the bed causes a mass movement of the fine solid toward the left. This causes the filter deposits to fall away from the dirty face, together with a small amount of the fine bed solids (see Figure 6 b). The central louvers are designed to prevent the coarse solids from participating in the movement of the fine solids toward the left. Efficiencies beyond 99.9 percent were observed in experiments for filtration of an aerosol of 1.1 micron particles through a sand bed.

The panel bed filter, with puffback cleaning, might also be used to absorb sulfur species from fuel gas or combustion products. A paper by Graff, et al. (7) discusses the potential of panel bed filters for simultaneous removal of fly-ash and sulfur dioxide with half-calcined dolomite at elevated temperatures. Other papers (8, 9, 10) discuss the possible use of panel bed filters for hydrogen sulfide removal from fuel gases at high temperatures. Again, half-calcined dolomite was considered. This process is patented by Squires (11).

In the case of hydrogen sulfide removal from fuel gas, the gas would flow horizontally across a bed of reactive solids. Each small space between the adjacent wishbone louvers constitutes a small reactor with countercurrent flow of granular solids and gas. The major advantages of panel bed filters for countercurrent contacting of gas and solids are predicted to be their compactness and their capability to operate at exceptionally small pressure drops. For a fuel gas having a face velocity of 0.15 m/s (30 ft/min), the panel bed can purify 183 m^3 of gas per minute per square meter of ground area (600 $ft^3/min/ft^2$). The ground area occupied by such a panel bed filter is comparable to that of a fluidized bed operating at a superficial velocity beyond 3 m/s (10 ft/s). The relatively low pressure drop across a panel bed filter is generally on the order of 2500 Pa (10 inches of water).

Figure 7 illustrates the CCNY Process (11). A combined flow of fuel gas, produced by gasification of coal or residual oil, and calcium carbonate or lime, is introduced into the panel bed filter. The fuel gas of reduced sulfur content then leaves the other end of the panel bed filter. Solids spilled by puffback pass to a separator, where coarse granular particles are separated from the finer particles and returned to the panel bed filter via a hopper. Spent fine particles containing calcium sulfide are reacted with water and carbon dioxide gas to produce a stream rich in hydrogen sulfide. The regenerated calcium carbonate particles are treated before being introduced into the hot fuel gas. If the fuel gas is sufficiently hot and has low carbon dioxide partial pressure, so that calcium carbonate is calcined when introduced in the gas, then the treatment consists only of drying. However, if it is not sufficiently hot enough to calcine calcium carbonate (above approximately 649°C, i.e. 1200°F), then the treatment includes slaking as well as calcination. If the fuel gas is at a substantially elevated pressure, greater than about 4×10^5 Pa (4 atm), the sulfided particles are reacted with steam and carbon dioxide at a temperature below about 704°C (1300°F). Other candidate solids for absorption of hydrogen sulfide from a fuel gas at elevated pressure include a composite of iron oxide and fly-ash, fully-calcined dolomite,

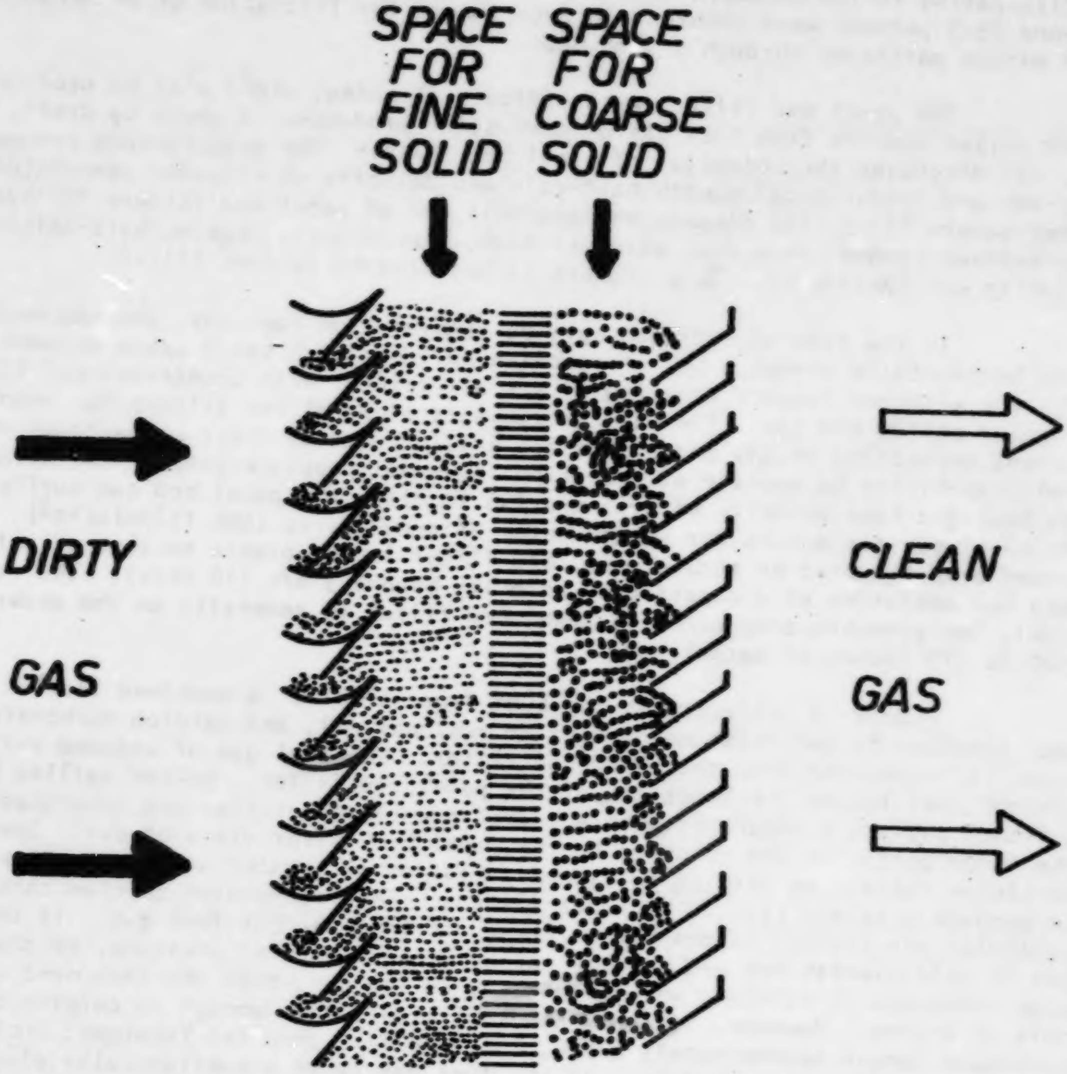

SPACE FOR FINE SOLID
SPACE FOR COARSE SOLID
DIRTY GAS
CLEAN GAS

FIGURE 5. CROSS SECTION OF PANEL BED FILTER

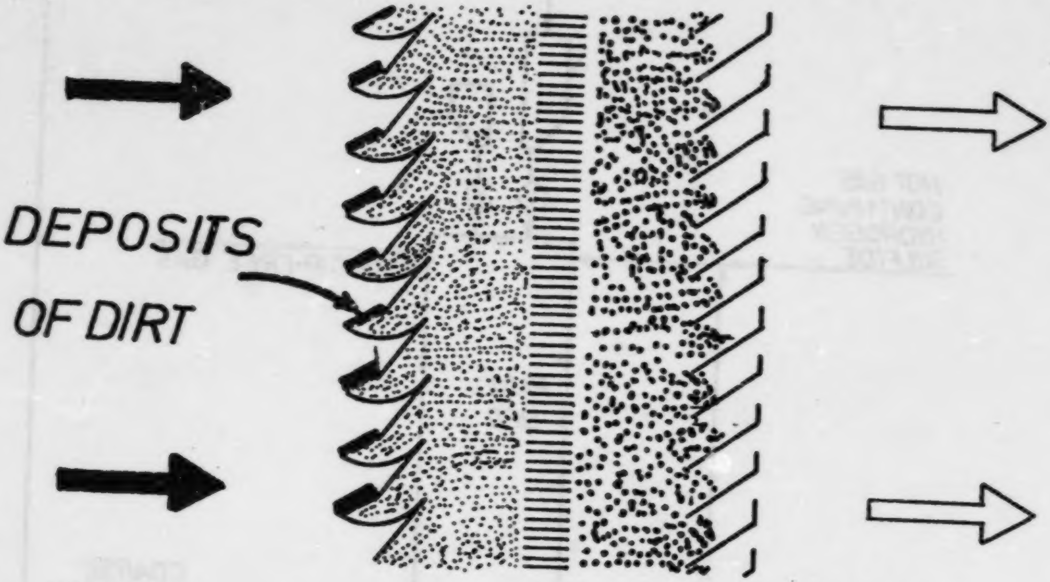

DEPOSITS
OF DIRT

FIGURE 6a. GAS CLEANING

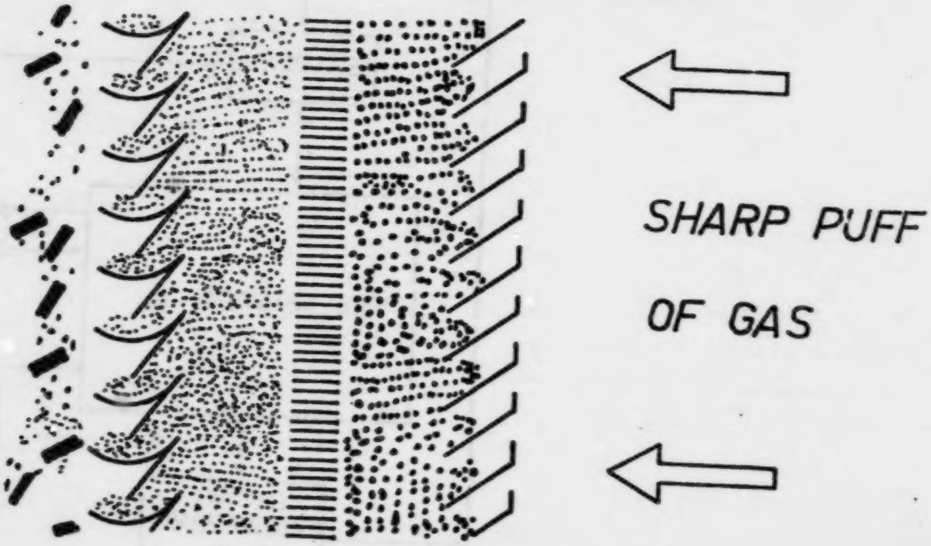
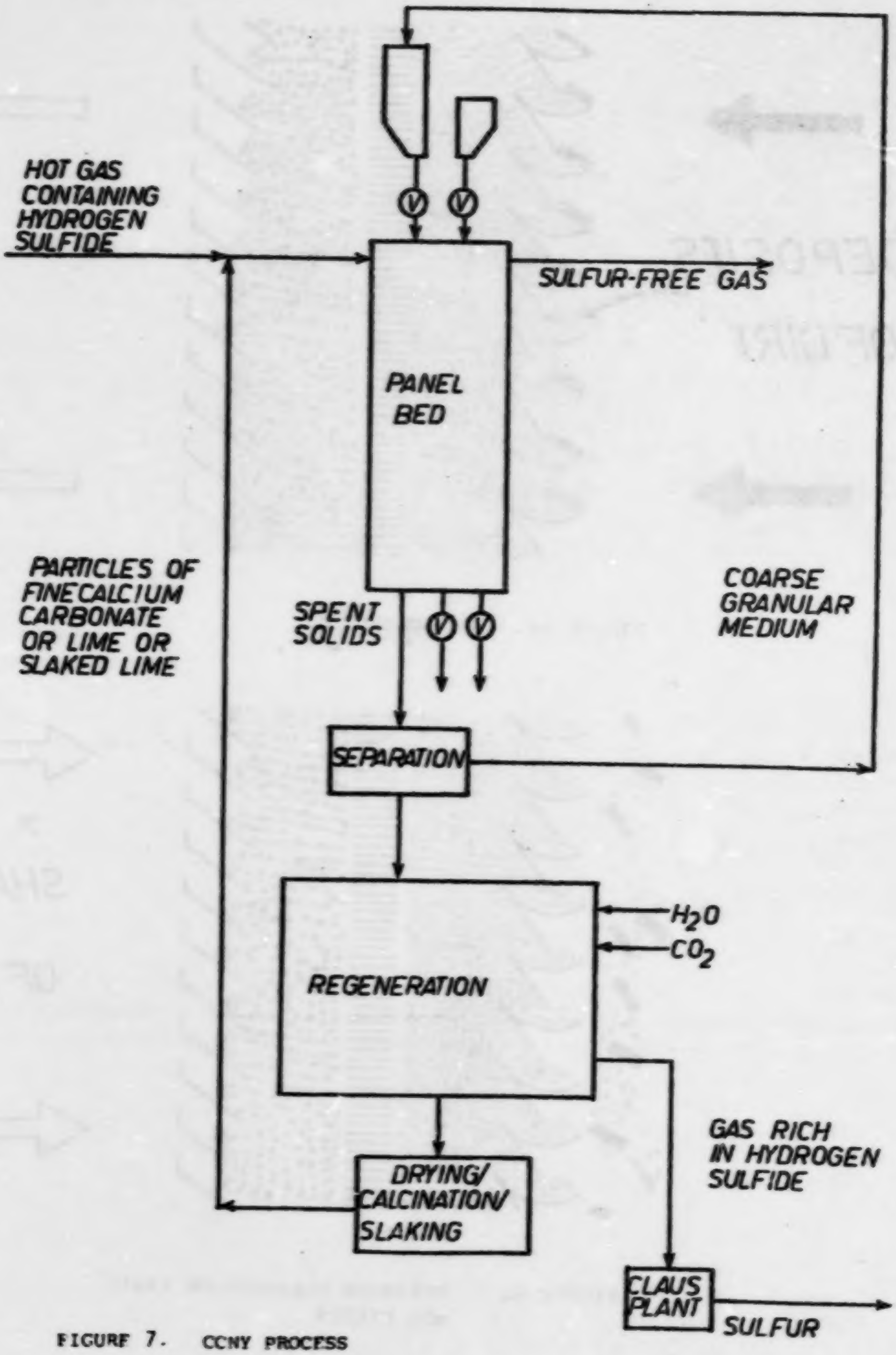

SHARP PUFF
OF GAS

FIGURE 6b. PUFFBACK CLEANING OF PANEL BED FILTER



HOT GAS CONTAINING HYDROGEN SULFIDE
V
V
SULFUR-FREE GAS
PANEL BED
PARTICLES OF FINECALCIUM CARBONATE OR LIME OR SLAKED LIME
SPENT SOLIDS
V
V
COARSE GRANULAR MEDIUM
SEPARATION
REGENERATION
H_2O
CO_2
GAS RICH IN HYDROGEN SULFIDE
DRYING/ CALCINATION/ SLAKING
CLAUS PLANT
SULFUR

FIGURE 7. CCNY PROCESS

and half-calcined dolomite (8).

Various design configurations for panel bed filters were studied through computer simulations (6). The results show that granular solids used to filter dust from gas might also advantageously serve as the active reagent for absorbing sulfur from the gas at atmospheric pressure. However, Squires does not recommend use of the panel bed filter for simultaneous sulfur and particulate removal in a single panel bed, especially at high pressures (A-2).

In addition to his involvement in the panel bed process, Squires has also studied desulfurization of fuels with fully- or half-calcined dolomite. A patent of Squires (12) describes a process whereby a fuel gas is desulfurized with fully- or half-calcined dolomite, and the sulfided dolomite is then reacted with steam and carbon dioxide at an elevated temperature and pressure to yield hydrogen sulfide and half-calcined dolomite. Hydrogen sulfide can then be converted to sulfur in a Claus plant. The results of lab-scale kinetic studies of sulfur absorption by dolomites are presented in several publications (13,14,15,16). The reasearch program on the panel bed filter for particulate removal has been terminated at CCNY. Further development is believed to be beyond the university research level (A-2). There are no futher plans at CCNY to develop and test the panel bed filter for sulfur removal (A- 3).

- Uncertainties and Problems: Since no experimental testing was performed with a panel bed for H_2S removal, the operation of this device remains highly uncertain for desulfurizing hot gases. An obvious potential operational problem involves the separation of sulfided absorbents from solid particles deposited on the bed. Other potential problems would include those observed under other processes with similar solid absorbents, such as poor regenerability and decreasing activity of absorbent. Although panel beds as solid filters have undergone considerable testing, they need to be experimentally proven for desulfurizing fuel gases at elevated temperatures.

3.1.1.4 CONOCO Process: Development of the CONOCO Process (17,18) by the Consilidated Coal Company was initiated in 1972 as an adaptation of the CO_2-Acceptor Coal Gasification Process. This research project was funded by the Environmental Protection Agency until it was terminated in 1976. There are no plans for further process development due to lack of funding.

The CONOCO Process was initiated when it was concluded that there was no real advantage in using the CO_2-Acceptor reaction together with a sulfur-acceptor reaction in the gasifier, when low-Btu fuel gas was the desired product. Desulfurization was then studied as a separate operation, outside the gasifier, by passing the low-Btu gas through a fluidized bed of half-calcined dolomite ($MgO.CaCO_3$). The H_2S absorption reaction is:

$$MgO.CaCO_3 + H_2S = MgO.CaS + H_2O + CO_2.$$

The kinetics of this reaction were also studied by Squires (19).

Figure 8 shows the variation of the equilibrium constant for the above reaction with temperature. Since the reaction is endothermic, hydrogen sulfide removal is favored at higher temperatures. On the other hand, the bed temperature should be held below the calcination temperature of the $CaCO_3$, which is dependent on the carbon dioxide partial pressure in the low-Btu gas. The calcination reaction is:

$$MgO.CaCO_3 = MgO.CaO + CO_2 .$$

The equilibrium relationship for the $CaCO_3$-CaO-CO_2 system is shown in Figure 1 of Section 1 (Air Products Process). The regeneration reaction is the reverse of the absorption reaction. It is favored by low temperature and high carbon dioxide and steam partial pressure.

A schematic diagram of the CONOCO Process is shown in Figure 9. The hot fuel gas from the gasifier is desulfurized in the H_2S sorption bed, at 899°C (1650°F) and 1.52×10^6 Pa (15 atm), by the reaction discussed previously.

The sulfided acceptor is conveyed to the regenerator by continuously recycling a stream of CO_2 and steam. The regenerator is maintained by 704°C (1300°F) and 1.52×10^6 Pa. The sulfided acceptor is then regenerated by the reverse of the above desulfurization reaction. The regenerated acceptor is returned by gravity to the gas desulfurizer. Spent acceptor from the regenerator is treated with water and carbon dioxide in the Chance Reactors at about 93°C (200°F) and atmospheric pressure before disposal. The Chance reaction is:

$$MgO.CaS + 2CO_2 + H_2O = MgCO_3.CaCO_3 + H_2S.$$

The H_2S concentration in the regeneration off-gas is restricted by the equilibrium conditions of the regeneration reaction. This gas, containing 3.6 percent H_2S at 87 percent approach to equilibrium, is introduced into a liquid phase Claus Reactor at about 154°C (310°F) and 1.52×10^6 Pa, where it is contacted with hydrosulfurous acid from an SO_2 absorption column. The liquid phase Claus reaction is:

$$2H_2S + H_2SO_3 = 3S + 3H_2O.$$

Liquid sulfur produced in the reaction is separated from the water. Part of the product sulfur is burned to produce sulfur dioxide for absorption by water in the SO_2 absorption column. It should be noted that a conventional Claus plant is not employed because the H_2S concentration in the off-gas is too low.

Absorption and regeneration experiments were carried out in a bench-scale apparatus, where regenerated solids were continusouly recycled to the absorber. Bottled gases were used to simulate low-Btu producer gas, and the exit gas from the absorber was recycled to reduce the gas consumption. Sorbent consisting of 28 x 35 and 35 x 48 Tyler mesh sizes was introduced into a 7.6 cm diameter, type 304 SS absorber at a flow rate of 1.4-3.2 kg/h. The sorbent was fluidized with 8.5-17.7 normal m^3/h (300-625 SCFH) low-Btu gas, producing a bed of 46 cm in height. The operating temperature and pressure in the absorber were 871°C (1600°F) and 1.52×10^6 Pa (15 atm), respectively. The sulfided sorbent was continuously drawn from the absorber and fed to a 5 cm diameter regenerator, where the bed was fluidized with

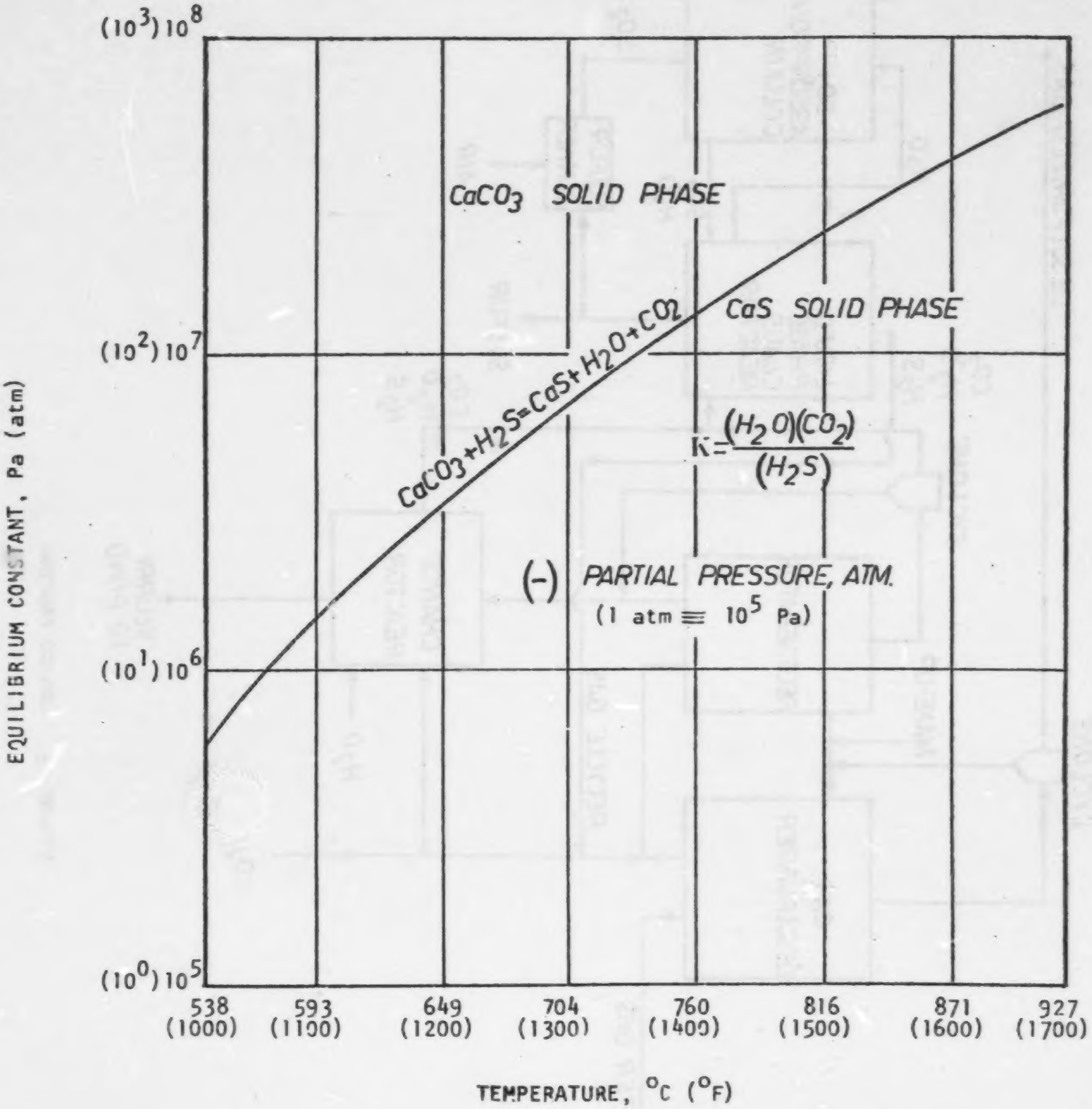


FIGURE 8. EQUILIBRIUM CONSTANT FOR THE REACTION OF H_2S with $CaCO_3$

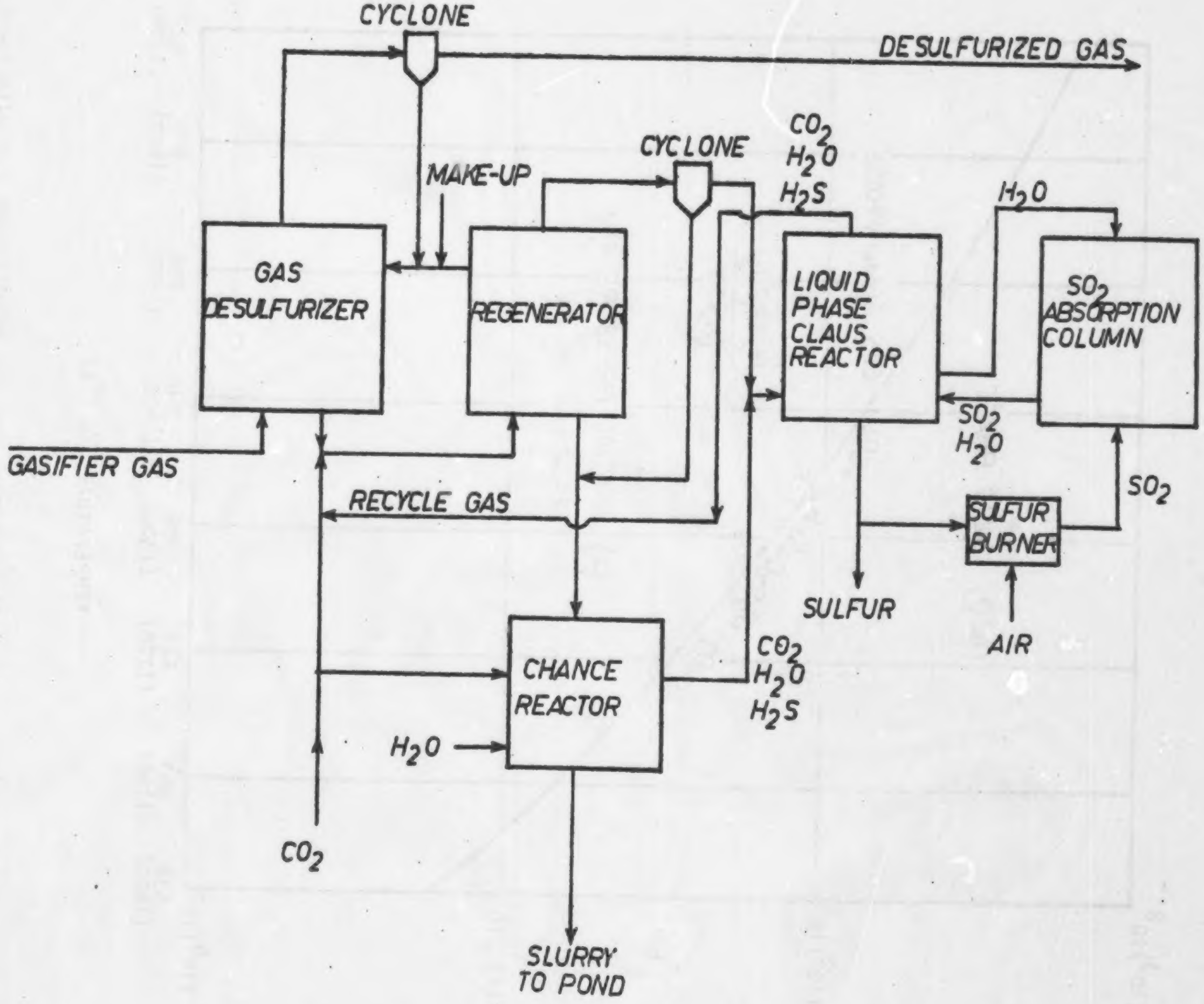

CYCLONE
DESULFURIZED GAS
MAKE-UP
CYCLONE
CO_2
H_2O
H_2S
H_2O
GAS DESULFURIZER
REGENERATOR
LIQUID PHASE CLAUS REACTOR
SO_2 ABSORPTION COLUMN
SO_2
H_2O
GASIFIER GAS
RECYCLE GAS
SULFUR BURNER
SO_2
SULFUR
AIR
CHANCE REACTOR
CO_2
H_2O
H_2S
H_2O
CO_2
SLURRY TO POND

FIGURE 9. CONOCO PROCESS

steam and carbon dioxide at 593-704°C (1100-1300°F) and 1.52×10^6Pa (15 atm) pressure. The regenerator bed height was maintained at 1.17 m.

Four types of dolomites (Tymochtee, Canaan, Pennsylvania and Virginia) and two types of limestones (Nebraska and 1691 from Seneca Falls, New York) were tested and evaluated. The Nebraska limestone showed little activity. While the 1691 limestone gave good attrition resistance, it formed agglomerates. Among the four dolomites tested, only Canaan stone, containing about 60 percent (by weight) CaO and 40 percent MgO, on oxide basis, had attrition rates less than 1 percent, acceptable activity, and long life. In the continous cycling studies (up to 37 cycles) with the Canaan dolomite, about 97 percent of the inlet H_2S was removed in the desulfurizer until most of the $CaCO_3$ was consumed. The decline in the regeneration activity was slow, and the H_2S concentration in the regeneration off-gas approached 75 percent of the equilibrium value. Increased levels of H_2S in the regeneration off-gas were observed at higher temperatures (e.g., 760°C as opposed to 704 or 593°C). The effect of solids make-up (about 5 percent under operating conditions) was tested, and the result verified with a computer model based on continuous runs with no make-up. Increase of particle size (20 x 28 vs. 35 x 45 Tyler mesh) did not have any effect on the sorbent activity.

Canaan dolomite was also tested with once-through operation to provide a basis for cost comparisons with process variations using regeneration. Hydrogen sulfide absorption of up to 96 percent was obtained with an 85-90 percent solids conversion. An attrition rate of about 1 percent of the solid feed was observed.

A hardening procedure was developed to reduce the attrition rates of soft dolomites. This procedure consisted of partially sulfiding the dolomite, oxidizing the sulfide to calcium sulfate, and introducing the sulfate to the absorber. The sulfate would then be reduced to sulfide under the operating conditions of the absorber. Continuous runs with hardened Tymochtee and Virginia dolomites gave attrition rates below 1 percent, but with some loss of regeneration activity.

Batch tests were conducted to develop a kinetic model of the overall process, and to determine the effects of various operating variables on desulfurization and regeneration. Regeneration was characterized as a "pseudo" first order process. The following variables were concluded to have no effect on outlet H_2S concentrations in the desulfurized gas: age of stone, particle size over the range 28 x 35 to 35 x 48 mesh, and inlet H_2S concentration over the range of 0.3 percent to 1.1 percent. Deeper beds and higher temperatures reduced the H_2S concentration and resulted in closer approaches to equilibrium. The percent regeneration of CaS decreased with increased stone age, and increased with increasing temperature and bed depth; it was also adversely affected by hardening of the stone. Cyclic studies revealed that high temperature regeneration was not useful as a reactivation method, since a large portion of the $CaCO_3$ produced was inactive in the absrober. Also, reduced residence time in the absorber improved the regeneration performance and cycle life.

Sulfur recovery from regeneration exit gas by the liquid phase Claus reaction was studied in a Jerguson sight gauge reactor, with an internal cross section of 1.6 cm x 191 cm and a length of 137 cm. The reactor was filled with glass beads of 3mm diameter. Experiments were carried out at 1.52×10^6 Pa pressure, and the temperature was kept in the range of 154-160°C (310-320°F) to prevent an increase in the viscosity of liquid sulfur above 160°C. Conversion of the feed sulfur (about 5.5 mole percent, 2/3 of which is H_2S and 1/3 SO_2) to elemental sulfur was experimentally demonstrated. In a run where 66.7 percent of the inlet sulfur was converted, the exit gas contained 1.2 percent H_2S and 0.1 percent SO_2, on a dry basis. In other runs, a larger reactor was simulated by making runs with inlet concentrations equal to outlet concentrations of previous runs.

The liquid phase Chance reaction was studied batch-wise in a glass apparatus, in two steps. In the first step, called hydrosulfidation, a slurry of CaS in water was treated with H_2S:

$$CaS + H_2S = Ca(HS)_2.$$

In the second step, called carbonation, CO_2 was introduced:

$$Ca(HS)_2 + CO_2 + H_2O = CaCO_3 + 2H_2S.$$

It was shown that, on a dry basis, about 95 percent sulfided sorbent, containing 26 percent sulfur, can be converted to a solid with 0.3 percent sulfur for disposal. The reaction was run at 91°C (195°F) and atmospheric pressure with a residence time of one hour.

- Uncertainties and Problems: The effect of temperature on sulfur removal efficiency needs to be studied further. Desulfurization tests were performed at 871°C (1600°F), with a hydrogen removal efficiency of about 97 percent being obtained. However, at higher temperatures not above the sorbent calcination temperature, improved sulfur removal efficiences would be expected because of the desulfurization reaction thermodynamics (Figure 8).

During the batch cycling studies, reduced residence time in the desulfurizer was found to improve the sorbent life. This fact has yet to be confirmed in continous runs. A reduced residence time would require smaller equipment, and a longer sorbent life would reduce sorbent make-up requirements.

A sulfur conversion of about 90 percent was estimated in the liquid phase Claus Reactor by the process developer. This estimate was obtained by extrapolating information gathered from various experimental runs. A single run, simulating the design conditions, would be more convincing. Furthermore, work is needed to define the optimum system with respect to reactor volume, gas concentration, temperature and mixing. There are also possibilities for improvements via the addition of catalysts and buffers, and operation with nonaqueous solvents.

Hardening of the two types of soft dolomite reduced the sorbent attrition rates with some loss of activity. Caution should be exercised in extrapolating limited experiment results when evaluating the applicability of various types of dolomites to the CONOCO Process. Similarly, the discouraging experimental results obtained with the two types of limestones should not be generalized for all types of limestones.

Corrosion was another problem encountered during operation. The inlet line to the desulfurizer and the body of the desulfurizer, which were originally made of type 310 SS, corroded. The inlet line was then replaced with a type 446 SS, and the desulfurizer with type 310 SS. No corrosion problems were encountered in the regenerator, which had a body and internals made of type 310 SS.

Coke formation in the desulfurizer might be a potential problem for the CONOCO Process. Although this problem was observed in the Air Products Process and was, in fact, one of the reasons for the termination of that research program, it was not observed in the CONOCO desulfurization studies. The desulfurizer in the CONOCO Process was run at about the same temperature range as in the Air Products Process, but at a higher pressure ($1.5x10^6$ Pa vs. $1x10^5$-$2x10^5$ Pa), which would normally favor coking. However, Air Products used higher CO and lower H_2O concentrations than CONOCO, which would enhance coking.

Finally, COS removal with the half-calcined dolomite was not experimentally studied by CONOCO, and thus remains an uncertainty.

3.1.1.5 U.S. Steel Process (A-4): U.S. Steel has been developing a process since 1973 to desulfurize coal-derived gas for use in the reduction of iron ore in a gravitating bed furnace operating at 816-982°C (1500-1800°F) and atmospheric pressure ($1x10^5$ Pa). Presently, natural gas is being used for this purpose. The process is internally funded and proprietary, and published information is not available. However, a patent application was recently submitted.

The U.S. Steel process employs fully-calcined dolomite (CaO.MgO) at temperatures above 816°C and atmospheric pressure. Sulfided sorbent is regenerated in a different method than the one used by Air Products and Chemicals, Inc. (which uses steam and carbon dioxide). This regeneration method is proprietary.

Bench-scale experiments were initially carried out for about six months. Bottled gases were used to simulate coal gas. The gas flow rate was varied between 1.7 and 3.40 normal m^3/h (60 and 120 SCFH).

Later, a small pilot plant was operated with a packed bed absorber, 3m high and 25 cm I.D., filled with fully-calcined dolomite. Coal gas was simulated by reforming natural gas, and then adding hydrogen sulfide. The 85 m^3/H at standard conditions (3000 SCFH), and the fixed bed was operated above 816°C and atmospheric pressure. Hydrogen sulfide removal efficiencies above 98.5 percent were achieved in these tests.

Further pilot plant tests are planned on gas from an existing gasifier.

- Uncertainties and Problems: Although the U.S. Steel Process is proprietary and no information on the operating problems is available, it can be anticipated that such problems as the deposition of tars and particualtes on the absorption bed would occur. This would decrease the sorbent activity and limit the type of dolomites that can be used for the process.

3.1.2 HGC Processes Using Iron Based Absorbents

Five HGC processes using iron based absorbents were identified. These processes are the Appleby-Frodingham, Babcock and Wilcox, Batelle Columbus Laboratories, IMMR and MERC Processes. Among these only the Appleby-Frodingham Process was ever used commercially. Currently, process research is being conducted only on the IMMR and MERC Processes, with work on the other processes having been terminated. The HGC processes using iron based absorbents are summarized below and in Table 3. Sections 3.1.2.1 through 3.1.2.5 present detailed information on these processes.

- Appleby-Frodingham Process: Hydrogen sulfide is absorbed with iron oxide (Fe_2O_3) at temperatures up to 427°C (800°F). Regeneration is with air. Three plants, two pilot and one full-scale, having daily capacities of 0.07×10^6, 0.110×10^6 and 0.906×10^6 m^3 of inlet gas, respectively, were operated in the United Kingdom in the 1950's and 1960's to purify coke oven and coal gases. Regeneration off gases containing sulfur dioxide were used to produce sulfuric acid. These plants were closed due to the availability of cheaper low-sulfur distillate fuels, as well as some operating problems.

- Babcock and Wilcox Process: Oxidized carbon steel (FeO) rods are used to absorb hydrogen sulfide from coal gases at temperatures between 427 and 649°C (800 and 1200°F). Regeneration is achieved with air at temperatures between 260 and 649°C (500 and 1200°F). Bench-scale and pilot plant tests were carried out to study the process feasibility. A conceptual design of the absorption-regeneration equipment was also developed. The research program was terminated in 1976 due to lack of internal funding.

- Battelle Columbus Laboratories Process: A mixture of iron oxide (Fe_2O_3), a proprietary material, and inerts (starch, bentonite, and sodium silicate) was tested at 538 and 816°C (1000 and 1500°F), and atmospheric pressure. Regeneration was achieved with air at 538°C (1000°C). Bench-scale experiments were terminated in 1975 due to lack of internal funding.

- IMMR Process: This process developed by the Institute for Mining and Minerals Research at the University of Kentucky removes sulfur compounds at high temperatures from fuel gases, with coal gasifier bottom ash (which contains iron oxide Fe_2O_3 as the active material) being employed as the absorbent. Regeneration of the spent absorbent is achieved with air. Bench-scale experiments were carried out at temperatures between 371 and 816°C (700 and 1500°F). This research program is ongoing.

- MERC Process: The Morgantown Energy Research Center, with support from Air Products and Chemicals, Inc. developed a process to desulfurize producer gases at temperatures between 538 and 816°C (1000 and 1500°F). A pelletized mixture of iron oxide (Fe_2O_3) and flyash or silica is employed as absorbent. The sulfided pellets are regenerated by oxidation with air at temperatures of 816°C. The larger-scale experimental work at MERC was indefinitely suspended upon review of the overall project by DOE. Instead, more basic research is being conducted.

TABLE 3 - HGC PROCESSES USING IRON BASED SOLID ABSORBENTS

HGC PROCESSES	STATUS	ABSORBENT	ABSORPTION TEMP. (°C)	PRESSURE (Pa)	GAS FLOW RATE normal m^3/H	METHOD OF REGENERATION	REGENERATION TEMPERATURE (°C)	COMMENTS
Appleby-Frodingham	Terminated	Fe_2O_3	360-427	$1x10^5$	$0.11x10^6$	Air	593-816	Commercial
Babcock & Wilcox	Terminated	FeO	427-649		170	Air	533-649	
Batelle Columbus	Terminated	Supported Fe_2O_3	538 816	$1x10^5$	0.06	Air	593	
IMMR	On-Going	Gasifier Ash (contains Fe_2O_3)	371-816	$4x10^5$ $9x10^5$	1.22	Air	427-649	
MERC	On-Going	Supported Fe_2O_3	538-816	$1x10^5$ $2x10^6$	212	Air	538-816	Experimental work suspended

3.1.2.1 Appleby-Frodingham Process: With the increasing use of coke oven gas in steel furnaces in the 1930's and 1940's, the Appleby-Frodingham Steel Company of England developed a high temperature sulfur removal process for coke oven gases for use in the production of low sulfur steels. At that time, the commercially available process for removing hydrogen sulfide was through the use of iron oxide purification boxes. This process operated at low temperatures (approximately 35°C (95°F) and suffered from high capital costs, large space requirements for installation, dirty handling problems, and a lack of an available market for the spent oxide. The process developed and tested by the Appleby-Frodingham Steel Company used iron oxide particles to absorb sulfur at temperatures between 343 and 399°C (650 and 750°F).

Laboratory-scale experiments (18) at Appleby- Frodingham were carried out between 1946 and 1948, and were later resumed in 1953. Absorption of both hydrogen sulfide and organic sulfur was studied using 16 mesh iron oxide particles at temperatures up to 699°C (1290°F) and at space velocities above 3000 per hour. Regeneration of the sulfided ore was achieved by means of air at temperatures up to 799°C (1470°F). The laboratory tests indicated high absorption rates and good activity of the absorbent over hundreds of cycles.

As a result of these favorable laboratory tests, a pilot plant was installed at Scunthorpe, and the first hot desulfurization tests began in mid-1956. The pilot plant purified approximately 0.071×10^6 m3 ($2.5 \times 10^6 ft^3$) of coke oven gas per day in a continous operation. During operation, raw coke oven gas was heated to about 249°C (480°F) by heat exchange with the purified coke oven gas, and was admitted to the bottom of a two-stage fluidized-bed absorber which used iron oxide particles as the absorbent. The coke oven gas was heated to 380°C (716°F) in the absorber by means of heat exchange with the hot ore from the regenerator. The sulfided ore was regenerated by fluidizing with air at temperatures between 600 and 800°C, yielding an effluent gas containing sulfur dioxide. The flow of solid materials between the absorber and regenerator was achieved through fluidization of the absorbent by means of air or an inert gas. The temperature of the pilot plant was self-sustaining once the plant started up. The degree of desulfurization attained in the pilot plant was only slightly lower (71 percent to 84 percent) than that achieved in the laboratory unit at similar space velocities and temperatures. However, 96 percent to 99 percent desulfurization of the coke oven gas was achieved by using two absoprtion beds in series. Removal of a portion of the organic sulfur was also observed.

As a result of the performance of the laboratory and pilot plant tests, a full scale desulfurization plant, with a daily capacity of 0.071 million cubic meters ($32 \times 10^6 ft^3$) of crude coke oven gas, was installed at Scunthorpe. This plant was equipped with a unit for the manufacture of sulfuric acid from the sulfur removed from the coke oven gas. The installation was designed to remove 90 percent of the hydrogen sulfide in the crude gas in a two-bed absorber, with the final equivalent production of 98 percent sulfuric acid.

Another plant was built to desulfurize 0.110 million normal m^3/day (3.9 million SCF/day) of coal gas at the Exeter Works of the South Western Board of England.

The anticipated performance was that approximately 99 percent of hydrogen sulfide would be removed, together with 90 percent of all organic sulfur compounds other than thiophene, of which 20 percent would be removed.

The schematic diagram in Figure 10 represents one of the three parellel units of the Appelby-Frodingham desulfurization plant at Exeter. Two such units were used in operation, keeping the third on standy-by.

The crude coke gas, from the main blower, is first heated by means of purified coke oven gas in a shell and tube heat exchanger, after which it is introduced to the base of the four-stage absorber. As the gas moves upward in the absorber, it fluidizes iron particles at each stage. The iron oxide in the absorber bed reacts with the hydrogen sulfide. The purified exit gas passes first through cyclones, then the heat exchanger for cooling, and finally, the multicyclone for dust removal. The iron sulfide from the absorber flows through two seals in series, where it is fluidized with an inert gas produced from the combustion of towns gas. It is then conveyed to the regenerator by means of SO_2-containing recycle gas from the acid plant; air can also be used as an alternative. In the regenerator, iron sulfide is converted to oxide by means of air. The oxide flows to the two lower stages of the absorber by gravity through two seals in parallel. The proportion of recycled oxide passing to either of the two lower beds is determined by temperature requirements and adjusted by solids control valves. Hot sulfur dioxide gases at 421°C (790°F) pass from the regenerator through a cyclone for the removal of coarse carryover particles, and then to an outlet manifold. The combined gases are then passed through two cyclones for the removal of fine dust and are introduced, finally, into the sulfuric acid plant. Fresh oxide for make-up is stored in an overhead bunker and is diverted pneumatically to small hoppers located on the top of each absorber, where it is introduced to the top stage of the absorber.

A.C. Bureau (21), et al, report that hydrogen sulfide removal at Exeter was 99.9 percent, which exceeded the design value of 99.0 percent. The organic sulfur removal, with the exception of thiophene, was the same as the design value of 90 percent. About 20 percent of thiophene was removed. The removal efficiency was strongly affected by the absorption temperature, with removal improving at higher temperatures and decreasing at lower temperatures. The inlet gas hydrogen sulfide concentration varied considerably between 7.16 and 14.64 g/m^3 (3.13 and 6.40 $grains/ft^3$) whereas the design value was 13.20 g/m^3 (5.77 $grains/ft^3$).

The capacity of each absorber was 0.110 million normal m^3/day (3.9×10^6 SCFD), with the amount of iron oxide fed to the plant varying between 1044 and 1453 kg/day (2,300 and 3,200 lbs/day) per absorber. Approximately 50 percent of the particle sizes were between 40 and 80 mesh, the rest being bigger.

The absorber was operated below 399°C (750°F). The temperature was 715-750°F at the bottom stage and 360-371°C (680-700°F) at the stage above the bottom. These two lower stages removed most of the sulfur, whereas the third stage contributed to sulfur removal only occasionally. The operating temperature in the regenerator was between 699 and 749°C (1290 and 1380°F) and the plant was self-supporting with respect to heat requirements. A slight loss of combustible constituents during the passage through the absorber was observed, as can be seen from Table 4.

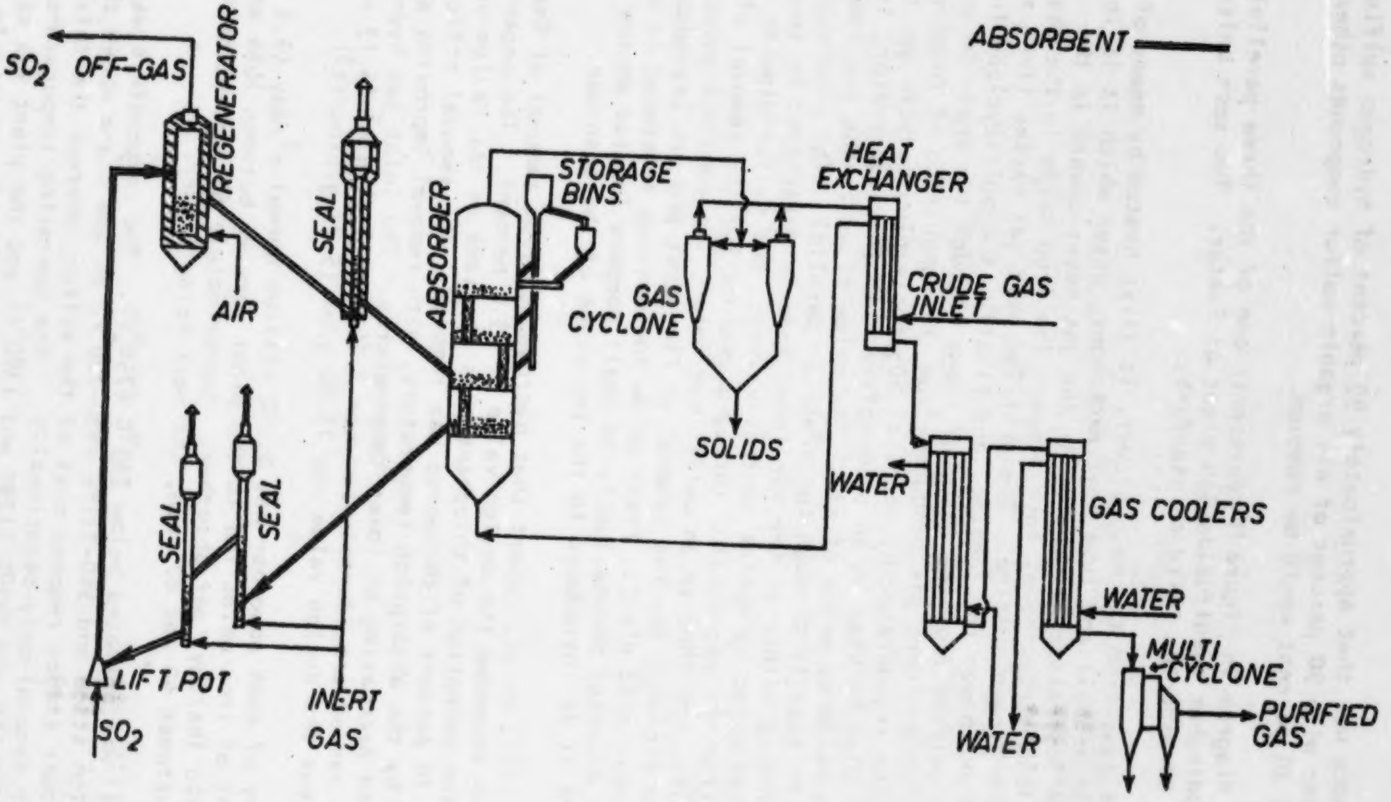

ABSORBENT
SO2 OFF-GAS
REGENERATOR
SEAL
AIR
ABSORBER
STORAGE BINS
GAS CYCLONE
SOLIDS
HEAT EXCHANGER
CRUDE GAS INLET
WATER
GAS COOLERS
WATER
SEAL
SEAL
LIFT POT
SO2
INERT GAS
WATER
MULTI CYCLONE
PURIFIED GAS

FIGURE 10. APPLEBY-FRODINGHAM PROCESS

Table 4

TYPICAL GAS ANALYSIS ACROSS AN ABSORBER

	Inlet (vol percent)	Exit (vol percent)
CO_2	4.8	5.0
C_nH_m	1.8	1.6
O_2	0.2	0.1
H_2	45.0	44.3
CO	15.1	14.7
C_2H_6	2.3	2.5
CH_4	15.4	15.4
N_2	15.4	16.4

About 90 percent of hydrocyanic acid present in the inlet gas, at 0.57-1.14 g/m^3 (0.25-0.50 grains/ ft^3) concentration, was converted to ammonia, which was subsequently removed at the exit of the desulfurization plant.

Loss of iron oxide from the plant varied between 7.6-10.9 g/m^3 (474 and 678 lb/10^6SCF) of coke oven gas. Loss of coke oven gas through the seals amounted to 0.5-1 percent of the inlet gas.

Because the oxide particles were conveyed by means of air instead of sulfur dioxide, the sulfur dioxide concentration in the gas to the acid plant was reduced to 3.5-6 percent, as compared to the design value of 10 percent.

The closure of the plant in March 1965 was primarily due to economic reasons such as the possibility of producing gas from light distillates at a lower cost than from solid fuels and the substantial reduction in the anticipated revenue from the sale of sulfuric acid. The problems involved with solids handling and the loss of iron oxide absorbent were also significant factors.

- Uncertainties and Problems: The following operating problems were observed at the desulfurization plants discussed above:

Absorbers: Loss of iron oxide was observed in the absorbers from the ends of the joints between the separate sections of the distribution plate. This was corrected by welding.

Indirect Coolers: Condensation took place in the hot gas section of the indirect coolers. This was corrected by use of a water seal. Although condensation in the cold gas section of the indirect coolers was minor, back-pressure built up in the cooler tubes causing occasional shut down of the plant. This was corrected by a spray of water.

Gas Multicyclones: Condensation in the gas multi-cyclones caused sludge build-up and blockage of tubes. This difficulty was solved by maintaining the temperature of the inlet gas above the water dewpoint.

Expansion Bellows: Expansion bellows were installed in the piping between the absorber, the regenerator, and the seals. These bellows failed and caused shut down of the plant due to the temperature differences, the corrosion by sulfur dioxide and trioxide, and the vibration of the fluidized equipments. This difficulty was solved through an improved bellows design.

Seals: An expansion chamber and a baffle plate were installed after carryover of fluidized particles in seals was observed.

Sulfur dioxide mains: The hot gas valves on the regenerator off gas main were affected by high temperatures, presence of sulfur oxides, and iron oxide dust. For these reasons, they did not operate properly.

Instruments: Some of the instruments, especially pressure and flow instruments, did not work as desired because of fluctuations caused by fluidization and the plugging of lines.

Oxide handling: Oxide losses, due to the small particle sizes, were greater than anticipated and resulted in increased make-up requirements. Dust caused serious difficulties with blowers, hot gas valves and instruments. Plant shut down was experienced due to the erosion of bends and rotary feed valves.

3.1.2.2 Babcock and Wilcox Process: The Babcock and Wilcox (B & W) Process uses iron oxide to remove hydrogen sulfide from gases at high temperatures. Bench-scale experiments and pilot plant tests were carried out to study the process feasibility. A conceptual design of the absorption-regeneration equipment was also developed. However, the need for larger scale experimentation and a lack of funding resulted in termination of the research program in 1976 (A-5,A-6).

Bench-scale tests were performed by passing about 0.11 normal m^3/h bottle gas (simulated synthesis gas) containing 1 percent H_2S, 12 percent CO, 8 percent CO_2, 1 percent CH_4 and 78 percent N_2 through the reactor bed. Two absorbent materials were tested: (1) sintered iron oxide, fabricated in the form of cyclindrical cells of 6.35 mm I.D. and 26.7 cm length, used at temperatures of 441 and 649°C (825 and 1200°F); and (2) carbon steel, used in annular (53 cm long and 9.5 mm threaded rod in 12.7 mm I.D. pipe) and tubular (6.8 mm I.D. and 1.98 m long) arrangements at 649 and 871°C. The reactants were heated in air at temperatures to 760°C (1400°F) to develop a thin surface layer of FeO_x:

$$Fe/Fe + Air \longrightarrow Fe/FeO_x + N_2$$

and were used to absorb hydrogen sulfide from the synthesis gas:

$$Fe/FeO_x + xH_2S \longrightarrow Fe/FeS_x + xH_2O.$$

Figure 11 shows the equilibrium constant for the H_2S absorption reaction:

$$FeO + H_2S = FeS + H_2O.$$

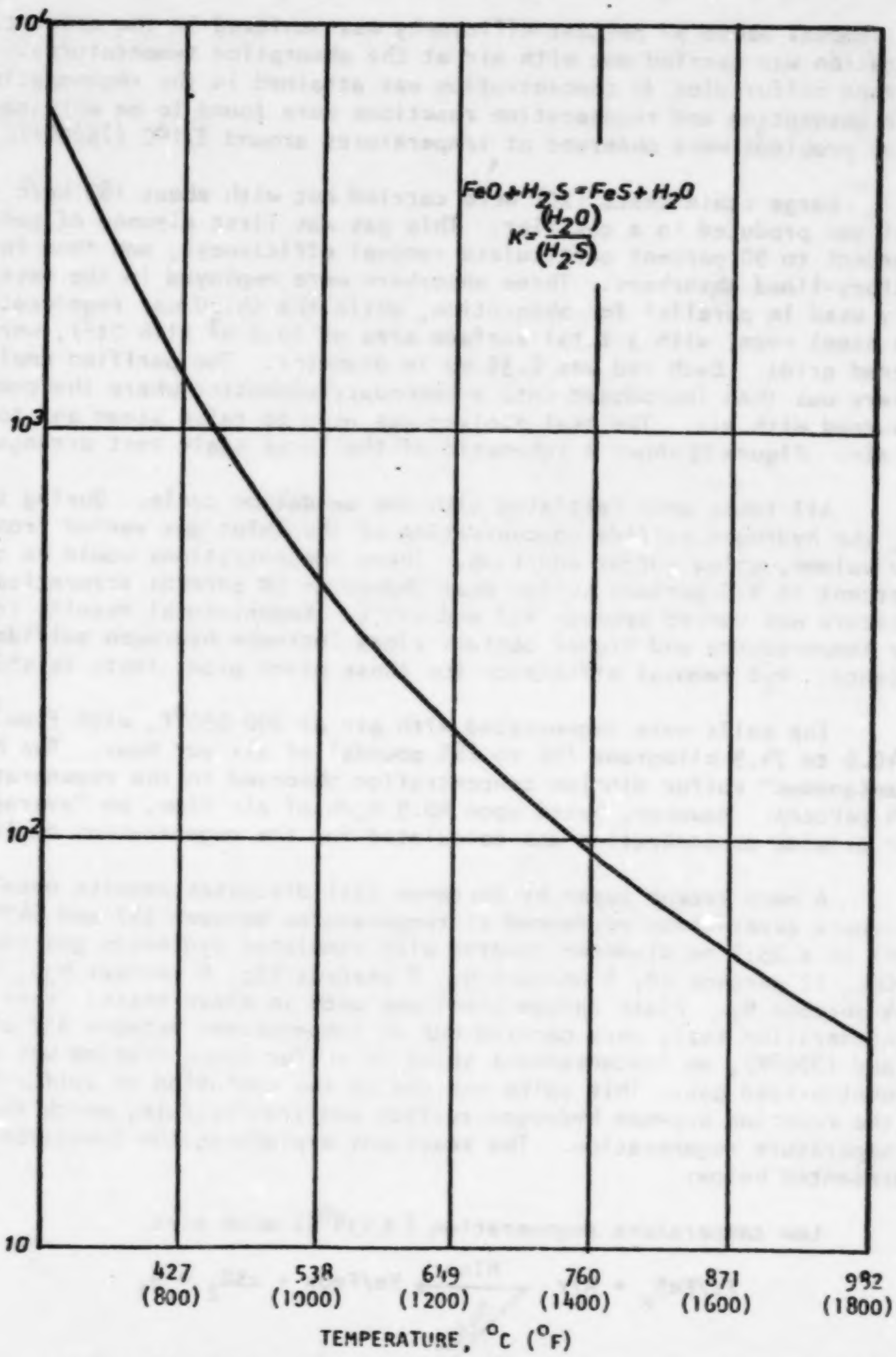


FIGURE 11. EQUILIBRIUM CONSTANT FOR H_2S ABSORPTION BY IRON OXIDE

Sulfur removal above 97 percent efficiency was achieved in the absorption tests. Regeneration was carried out with air at the absorption temperatures. Approximately 13 percent sulfur dioxide concentration was attained in the regeneration off-gas and the absorption and regeneration reactions were found to be very rapid. However, material problems were observed at temperatures around 871°C (1600°F).

Large scale tests (20) were carried out with about 182 kg/h (400 lb/h) of coal gas produced in a gasifier. This gas was first cleaned of particulates (80 percent to 90 percent particulate removal efficiency), and then introduced into refractory-lined absorbers. Three absorbers were employed in the tests, with two usually used in parallel for absorption, while the third was regenerated with air. Carbon steel rods, with a total surface area of 10.8 m^2 (116 ft^2), were arranged in staggered grids. Each rod was 6.35 mm in diameter. The purified coal gas from the absorbers was then introduced into a secondary combustor where the combustibles were burned with air. The heat evolved was used to raise steam and to preheat the inlet air. Figure 12 shows a schematic of the large scale test arrangement.

All tests were initiated with the oxidation cycle. During the absorption cycle, the hydrogen sulfide concentration of the inlet gas varied from 1000 to 7500 ppm by volume, using sulfur addition. These concentrations would be obtained from 0.6 percent to 4.5 percent sulfur coal (based on 50 percent theoretical air). The temperature was varied between 427 and 649°C. Experimental results indicate that higher temperatures and higher contact times increase hydrogen sulfide removal efficiency. H_2S removal efficiency for these pilot plant tests is shown in Figure 13.

The cells were regenerated with air at 500-650°F, with flow rates ranging from 40.9 to 74.9 kilograms (90 to 165 pounds) of air per hour. The highest "instantaneous" sulfur dioxide concentration observed in the regeneration off-gas was 14 percent. However, based upon 40.9 kg/h of air flow, an "average" 3.3 percent sulfur dioxide concentration was calculated for the regeneration cycle.

A more recent paper by Kertamus (21) discusses results obtained from bench-scale experiments performed at temperatures between 357 and 649°C (675 and 1200°F) in a 25.4 mm diameter reactor with simulated synthesis gas containing 1 percent CH_4, 12 percent CO, 8 percent H_2, 8 percent CO_2, 6 percent H_2O, 1 percent H_2S and 64 percent N_2. Plain carbon steel was used in these tests. When absorption and regeneration tests were carried out at temperatures between 357 and 538°C (675 and 1000°F), an instantaneous spike in sulfur concentration was observed in the desulfurized gas. This spike was due to the evolution of sulfur dioxide formed from the reaction between hydrogen sulfide and iron sulfate, which resulted from low temperature regeneration. The reactions explaining the formation of the spike are presented below:

Low temperature regeneration ($<538^\circ C$) with air:

$$\begin{tikzcd}
\mathrm{Fe/FeS_x + Air} \arrow[r, "\mathrm{Minor}"] \arrow[dr, "\mathrm{Major}"'] & \mathrm{Fe/FeOx + xSO_2 + N_2} \\
 & \mathrm{Fe/FeSO_4 + N_2}
\end{tikzcd}$$

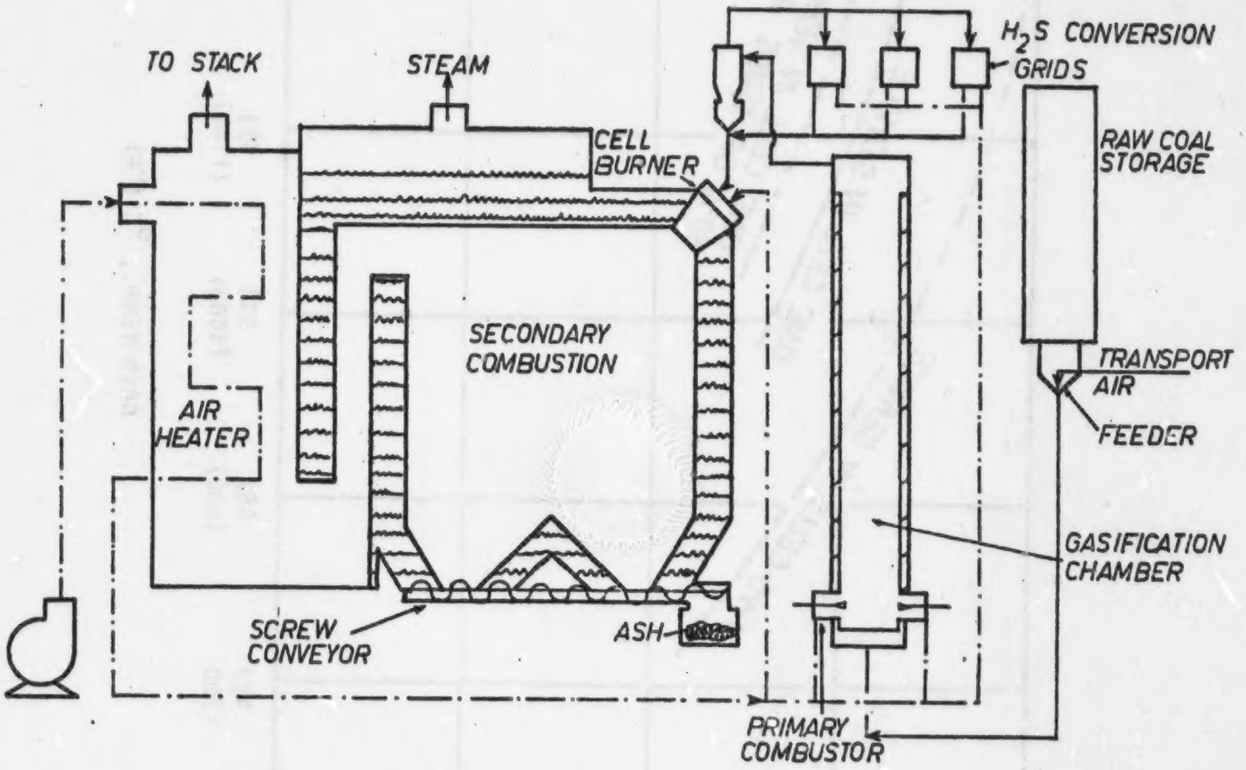

TO STACK
STEAM
H_2S CONVERSION GRIDS
CELL BURNER
RAW COAL STORAGE
SECONDARY COMBUSTION
AIR HEATER
TRANSPORT AIR
FEEDER
GASIFICATION CHAMBER
SCREW CONVEYOR
ASH
PRIMARY COMBUSTOR

FIGURE 12. LARGE SCALE TEST CONFIGURATION

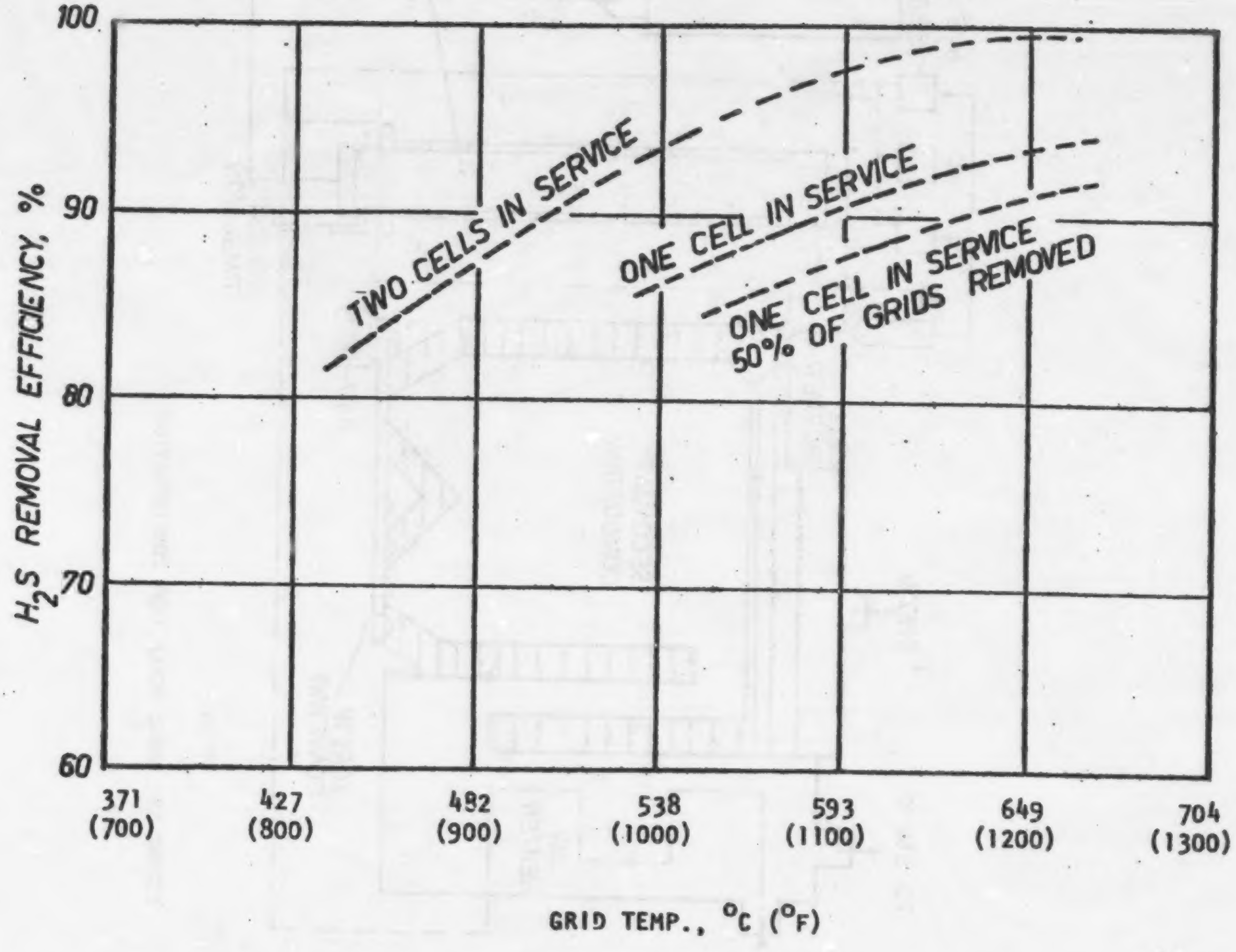


FIGURE 13. H_2S REMOVAL EFFICIENCY FOR LARGE SCALE EXPERIMENTS

Sulfur concentration spike:

$$Fe/FeSO_4 + 4/3\ H_2S \longrightarrow Fe/FeS + 4/3\ H_2O + 4/3\ SO_2$$

The formation of the spike was eliminated by raising the regeneration temperature above 538°C. Sulfur removal efficiencies in excess of 95 percent were observed at temperatures between 357 and 538°C and space velocities of 2000-2500 per hour. The absorption experiment was terminated when the H_2S concentration in the desulfurized gas reached 0.1 percent (end point). An average H_2S concentration in the desulfurized gas was then obtained at each absorption temperature. The results are given in Figure 14. Under the same operating conditions, sulfur removal increased linearly with temperature from 1.07 m^3 $H_2S/100$ m^2 surface (3.5 SCF $H_2S/100$ sq. ft. surface) at 357°C to 4.3 m^3 $H_2S/100$ m^2 surface (14 SCF $H_2S/100$ sq. ft. surface) at 538°C. This is shown in Figure 15.

The conceptual design of the absorption-regeneration equipment developed by B & W Co. consisted of a stainless steel cylindrical unit segmented into sixteen compartments. Each compartment is filled with carbon-steel plates oriented longitudinally with the gas flow, offering about 9.3 m^2 (100 ft^2) of surface area. Absorption takes place in thirteen of the sixteen compartments, while regeneration is being carried out in the remaining compartments. The regeneration air passes in and upward in the first compartment to a crossover, then downward for a second pass, and upward for a third and final pass. At two revolutions per hour, each of the sixteen compartments is regenerated twice per hour. The regeneration off-gas contains from 10 percent to 13 percent SO_2. The conceptual design is shown in Figure 16.

- Uncertainties and Problems: The process developer indicates that the optimum operating temperature is between 593° and 649°C (1100° and 1200°F). Operation at a higher temperature, 871°C (1600°F), resulted in unsuccessful regeneration, coupled with bending of the reaction tube due to the internal heat. However, no test was performed at temperatures between 649 and 871°C; therefore, the upper temperature limit is not clear. On the other hand, low temperature regeneration resulted in the formation of $FeSO_4$, which, after reaction with the coal gas in the desulfurizer, yielded sulfur dioxide gas. This was eliminated by operating above 538°C (1000°F).

Particle deposition on the grids can limit and even prevent the absorption and regeneration reactions. In fact, such a problem was observed in the pilot plant testing.

Carbonyl sulfide removal was not studied in these experiments and, therefore, remains an uncertainty.

The conceptual design of the absorption-regeneration equipment developed by B & W was not tested, and the technical and economic feasibility of this concept has yet to be demonstrated.

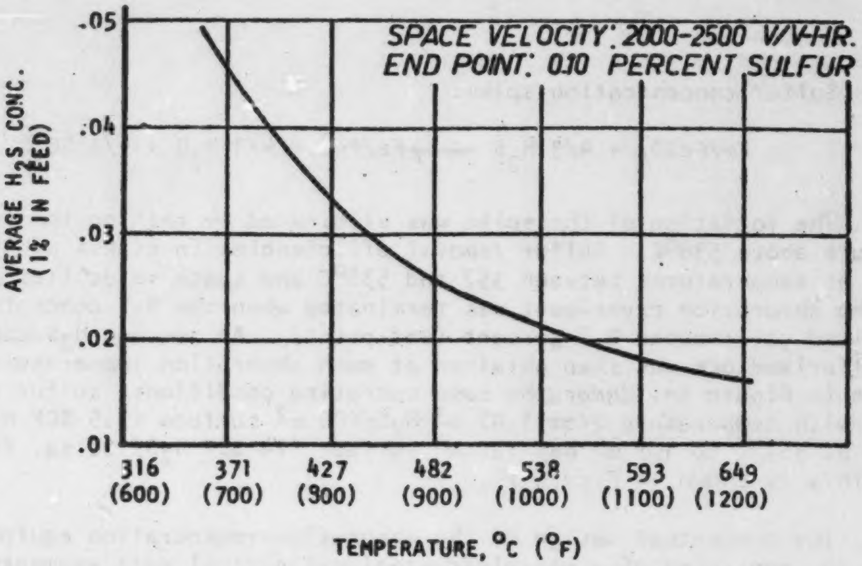


FIGURE 14. SULFUR CONCENTRATION VERSUS TEMPERATURE

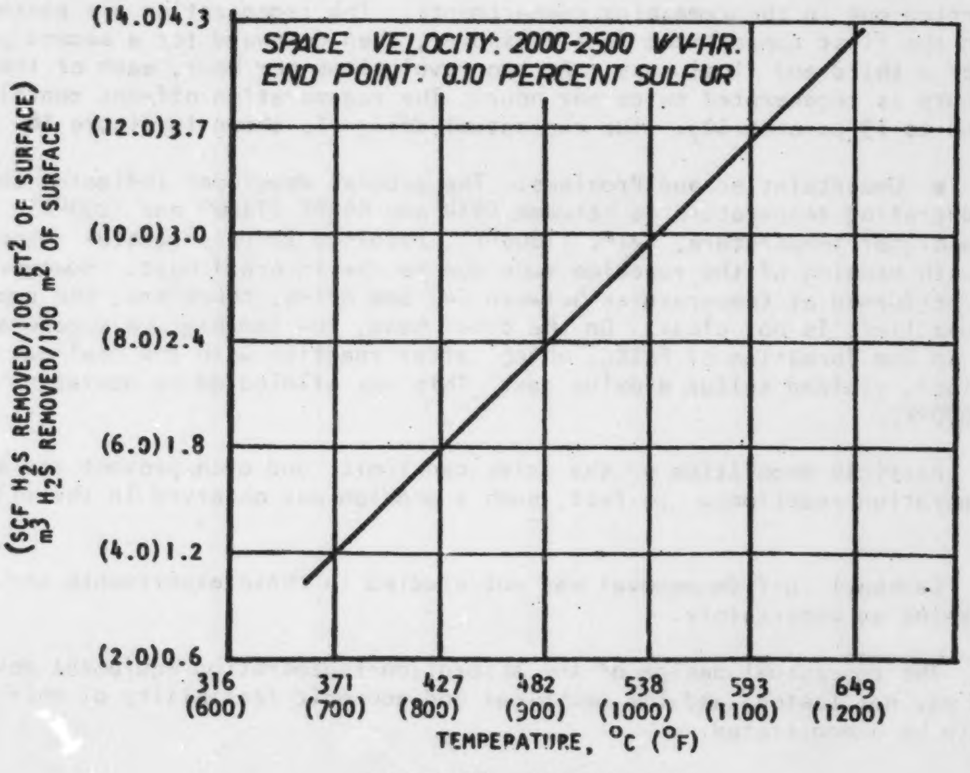


FIGURE 15. SULFUR REMOVAL

3.1.2.3 **Battelle Columbus Laboratories Process:** Battelle Columbus Laboratories (BCL) developed iron-oxide sorbents (22) to remove hydrogen sulfide from coal gases at elevated temperatures. Work at BCL began in 1974, as a result of funding under the Battelle Energy Program, but was suspended in late 1975 due to termination of this internal funding (A-7).

The sorbent contains a mixture of iron oxide and a proprietary material. This material is believed to react, to a limited extent, with hydrogen sulfide, and improves the overall reactivity of the sorbent. The absorption reaction of iron oxide with hydrogen sulfide can be explained through either of two mechanisms:

(1) According to ICI (23), fresh iron oxide (Fe_2O_3) is converted to Fe_3O_4, in the presence of hydrogen at temperatures above 177°C (350°F). The Fe_3O_4 then reacts with hydrogen sulfide to produce FeS, as follows:

$$3Fe_2O_3 + H_2 = 2Fe_3O_4 + H_2O$$

$$Fe_3O_4 + H_2 + 3H_2S = 3FeS + 4H_2O$$

(2) The U.S. Bureau of Mines (24) reports that the following reaction takes place:

$$Fe_2O_3 + 3H_2S = FeS + FeS_2 + 3H_2O.$$

The sorbent in the BCL tests was prepared by adding one gram each of starch, bentonite, and sodium silicate to 100 grams of a mixture of iron oxide and the proprietary material. The mixture was then either pelletized or extruded (the extrudates being 3.17 mm in diameter and 6.35 mm long), oven dried at 121°C (250°F), sintered at 871-982°C (1600-1800°F), and screened to remove all minus 10 mesh particles.

Laboratory-scale absorption tests were carried out in a fixed-bed tubular glass reactor of 5.1 cm diameter at 538 and 816°C (1000 and 1500°F) temperatures and atmospheric pressure. A glass (quartz) reactor was chosen after steel reactors (types 304 and 446) were found to react severely with hydrogen sulfide. Bottled gas containing 17 percent H_2, 26 percent CO, 5 percent CO_2, 50.5 percent N_2 and 1.5 percent H_2S(21.7 g H_2S/m^3 or 9.5 grains H_2S/ft^3 gas) was used to simulate coal gas. Approximately 16.52 normal cm^3/s (2.1 SCFH) of gas was passed over 100 grams of sorbent in each absorption test. The space velocity was 600 vol. gas/vol.bed/hr. Hydrogen sulfide removal efficiency was found to be above 97 percent, and was higher at 538°C than at 816°C. However, lower desulfurization efficiencies would be expected under the same operating conditions if steam were present in the inlet fuel gas. The sorbent developed by BCL proved to be superior to both pure iron oxide and iron oxide-fly ash mixture (developed by the U.S. Bureau of Mines) with respect to sulfur removal and attrition resistance.

Regeneration tests were performed at 538°C with an air flow rate of 16.52 normal cm^3/s. However, experimental data did not provide conclusive evidence with regard to the comparative regeneration characteristics of the various sorbents.

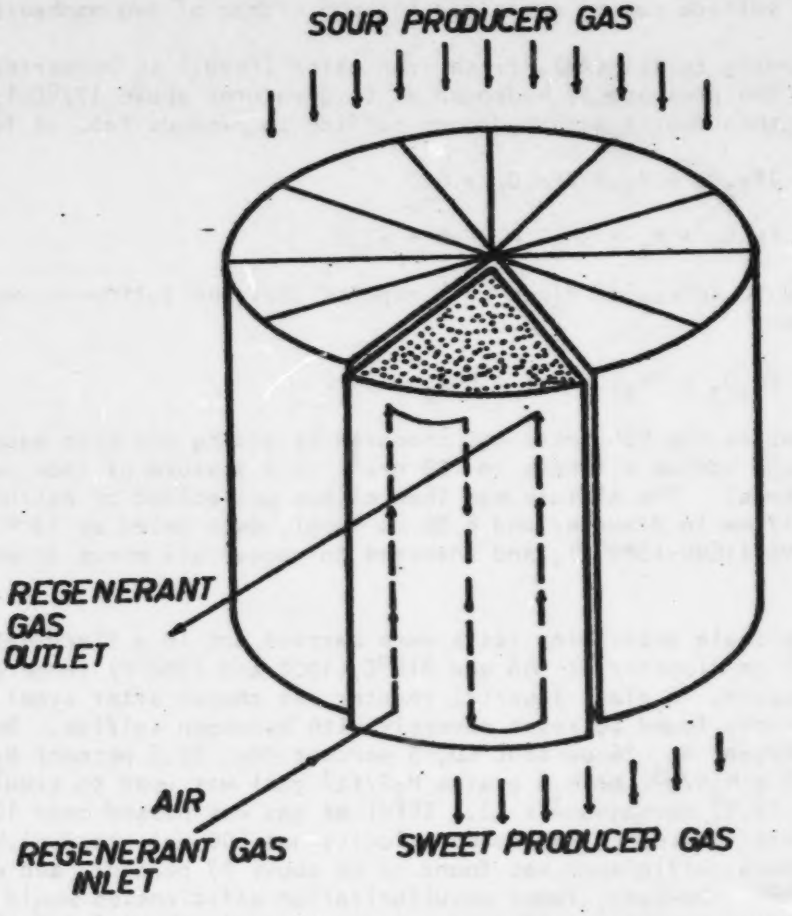

SOUR PRODUCER GAS
REGENERANT GAS OUTLET
AIR
REGENERANT GAS INLET
SWEET PRODUCER GAS

FIGURE 16. B & W REGENERATIVE DESULFURIZER

- **Uncertainties and Problems:** Severe corrosion was observed in the reactors fabricated from types 304 and 446 stainless steels. This experimental problem was solved by employing a quartz reactor. However, the type of material that can be used in larger scale applications remains uncertain.

The simulated coal gas used in the experiments did not contain any particles, tars, or steam. Particles present in actual coal gases might deposit on the absorbent surface, reduce the absorbent life, and even cause plugging of the bed. Desulfurization at lower temperatures (e.g. 538°C) might cause the condensation of tars. Also, lower desulfurization efficiencies would generally be expected than those obtained from these experimental runs, since steam is usually present in coal-derived product gases.

In view of the limited data on the regeneration step, the regenerability of the absorbent is uncertain.

3.1.2.4 IMMR Process: The process developed by the Institute for Mining and Minerals Research (IMMR) of the University of Kentucky uses the iron contained in coal ash as the absorbent for hot gas desulfurization. This research program, which was initiated in 1973, is ongoing and is being funded by the Department of Energy. Bench-scale tests were performed in fixed- and fluidized-bed reactors to develop and understand the basic chemistry of desulfurization, regeneration, and sulfur extraction, and to determine the important parameters and optimum operating conditions.

The primary desulfurization reactant in coal ash obtained from a high temperature oxidizing atmosphere is ferric oxide (Fe_2O_3). Under the reducing conditions of the desulfurizer, both reduction and desulfurization reactions take place. The reduction reactions are between the reducing gases (hydrogen and carbon monoxide) and iron oxides. These reduction reactions can be represented as follows:

$$3Fe_2O_3 + H_2 = 2Fe_3O_4 + H_2O \quad (1)$$

$$3Fe_2O_3 + CO = 2Fe_3O_4 + CO_2 \quad (2)$$

$$Fe_3O_4 + H_2 = 3FeO + H_2O \quad (3)$$

$$Fe_3O_4 + CO = 3FeO + CO_2 \quad (4)$$

$$FeO + H_2 + Fe + H_2O \quad (5)$$

$$FeO + CO = Fe + CO_2 \quad (6)$$

The principal desulfurization reactions are between hydrogen sulfide and ferric oxide, ferrous oxide and elemental iron:

$$Fe_2O_3 + 2H_2S + H_2 = 2FeS + 3H_2O \quad (7)$$

$$Fe_2O_3 + 4H_2S = 2FeS_2 + 3H_2O + H_2 \quad (8)$$

$$FeO + H_2S = FeS + H_2O \quad (9)$$

$$FeO + 2H_2S = FeS_2 + H_2O + H_2 \quad (10)$$

$$Fe + H_2S = FeS + H_2 \qquad (11)$$

$$Fe + 2H_2S = FeS_2 + 2H_2 \qquad (12)$$

Temperature has an effect on the forms of reactants and products. At 680°C (1256°F) ferric oxide transforms from alpha to beta, and at 780°C (1436°F) from beta to gamma. Ferrous sulfide transforms from alpha to beta at 280°F, and from beta to gamma at 325°C (617°F). Ferric disulfide (FeS_2) occurs in two crystalline structures: the cubic form (pyrite) and the rhombic form (marcasite). Marcasite transforms to pyrite at temperatures above 360°C (680°F).

Equilibrium curves for some of the above reduction and desulfurization reactions are shown in Figure 17. It can be seen that hydrogen sulfide removal is favored at lower temperatures. Total pressure has no effect upon the equilibrium conversions, since an equal number of moles of gas appear on each side of all reduction and desulfurization reactions.

Regeneration of the spent sorbent can be achieved with air, according to the following reactions:

$$4FeS + 7O_2 = 2Fe_2O_3 + 4SO_2 \qquad (13)$$

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2 \qquad (14)$$

Regeneration can also be achieved with sulfur dioxide, with sulfur being extracted. These reactions are:

$$6FeS + 4SO_2 = 2Fe_3O_4 + 5S_2 \qquad (15)$$

$$3FeS_2 + 2SO_2 = Fe_3O_4 + 4S_2 \qquad (16)$$

Reactions (13) and (14) are exothermic, and have very large equilibrium constants ($\mathcal{K} > 10^{100}$) at temperatures between 371 and 816°C (700 and 1500°F). On the other hand, reactions (15) and (16) are endothermic. The equilibrium constants for reactions (15) and (16) are very small, as shown in Table 5.

Table 5 - EQUILIBRIUM CONSTANTS FOR REACTIONS (15) and (16)

Temperature (K)	Equilibrium Constants Reaction (15)	Equilibrium Constants Reaction (16)
650	1.94×10^{-13}	2.00×10^{-10}
800	2.88×10^{-11}	2.21×10^{-13}
950	1.21×10^{-9}	8.43×10^{-8}
1100	2.0×10^{-8}	1.01×10^{-3}

Fixed-bed experiments (25,26) were carried out in a 5 cm I.D., 1.22 m long, 442 stainless steel reactor with the bed height being varied between 79 cm and 122 cm. The sorbent was a Western Kentucky No. 9 coal ash from a fixed-bed gas producer,

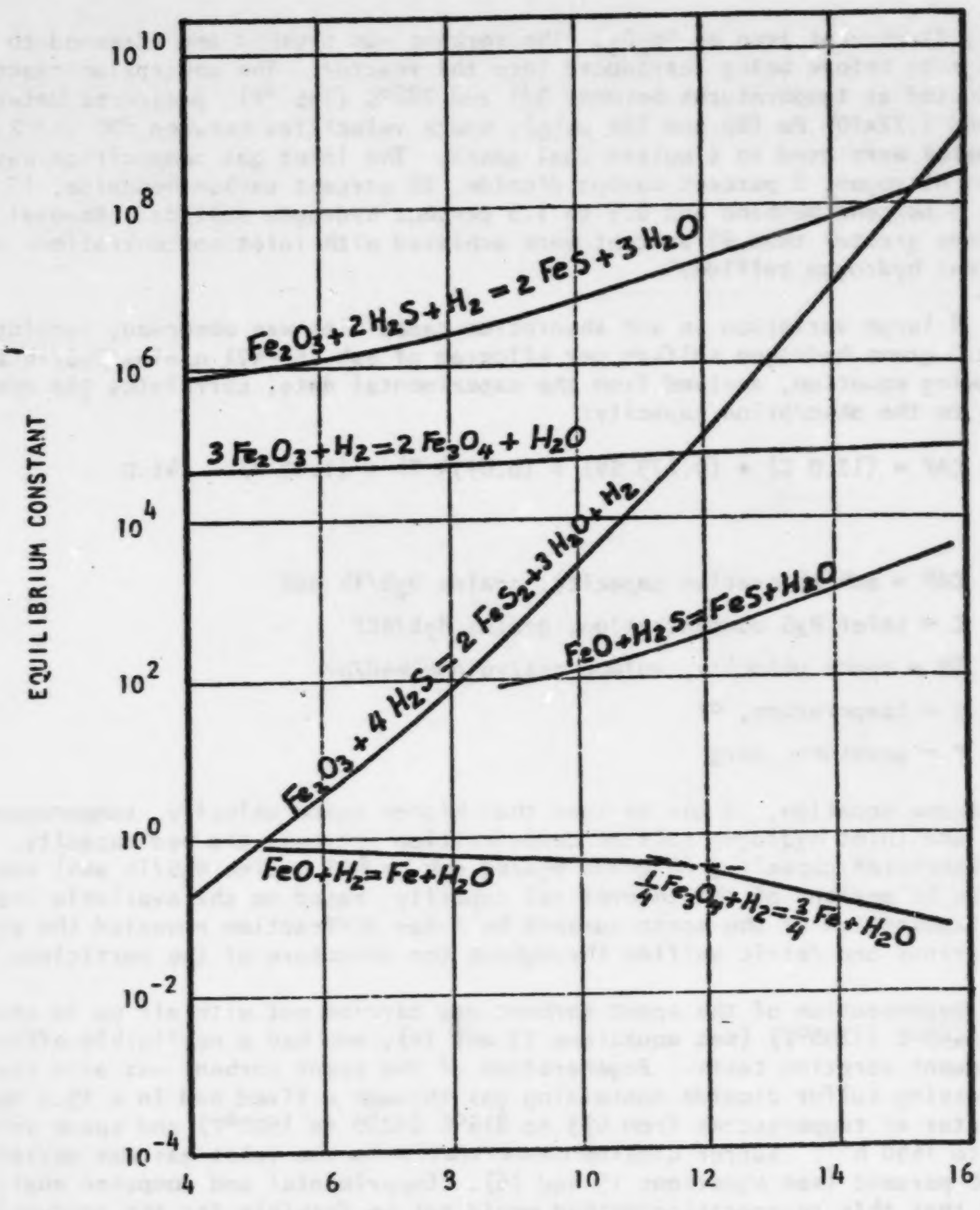


FIGURE 17. EQUILIBRIUM CONSTANTS FOR REDUCTION AND DESULFURIZATION REACTIONS

containing 23 percent iron as Fe_2O_3. The sorbent was crushed and screened to a 3x16 mesh size before being introduced into the reactor. The absorption reactions were conducted at temperatures between 371 and 788°C (1450°F), pressures between 6.5×10^5 and 1.22×10^6 Pa (80 and 150 psig), space velocities between 800 and 2,000h^{-1}. Bottled gases were used to simulate coal gases. The inlet gas composition was: 53 percent nitrogen, 8 percent carbon dioxide, 20 percent carbon monoxide, 15 percent hydrogen, 3 percent methane and 0.5 to 1.5 percent hydrogen sulfide. Removal efficiencies greater than 99 percent were achieved with inlet concentrations up to 1.25 percent hydrogen sulfide.

A large variation in ash absorption capacities was observed, ranging from 8.3 to 60.0 grams hydrogen sulfide per kilogram of ash (58-421 grains H_2S/lb ash). The following equation, derived from the experimental data, correlates the operating variables to the absorption capacity:

$$CAP = (12.0\ C) + (0.173\ SV) + (0.0974\ T) + (1.42\ P) - 341.0$$

where

CAP = ash absorption capacity, grains H_2S/lb ash

C = inlet H_2S concentration, grains H_2S/SCF

SV = space velocity, volume gas/volume bed/hr

T = temperature, °F

P = pressure, psig

From the above equation, it can be seen that higher space velocity, temperature, pressure, and inlet hydrogen sulfide concentration increase the bed capacity. The highest absorption capacity, 60 grams H_2S/kg ash or (421 grains H_2S/lb ash) was found to be 61 percent of the theoretical capacity, based on the available iron in ash. Examination of the spent sorbent by X-Ray diffraction revealed the presence of both ferrous and ferric sulfide throughout the structure of the particles.

Regeneration of the spent sorbent was carried out with air up to seven cycles at 649°C (1200°F) (see equations 13 and 14), and had a negligible effect on the subsequent sorption tests. Regeneration of the spent sorbent was also studied (27) by passing sulfur dioxide containing gas through a fixed bed in a 19.1 mm I.D. glass reactor at temperatures from 693 to 816°C (1280 to 1500°F) and space velocities from 430 to 1690 h^{-1}. Sulfur dioxide concentration in the inlet gas was varied between 22 and 100 percent (see equations 15 and 16). Experimental and computer analysis suggested that this regeneration method would not be feasible for the production of elemental sulfur. The primary reason is due to the low equilibrium constants, requiring large quantities of sulfur dioxide for recycle. At 727°C (1340°F) and 20 percent SO_2 in the feed gas, a circulation load of 77 m^3/kg (6×10^6 ft^3 per ton) of sulfur produced would be required. In addition, the product gas stream would be cooled for sulfur condensation and then reheated, resulting in an energy loss. Furthermore, recycling of large gas volumes would cause increased pumping costs.

Fluidized-bed desulfurization (26) was also investigated in a glass tube reaction of 5 cm I.D. and 91 cm height, by passing a mixture of bottled gases through the bed. The gas mixture contained hydroden, carbon monoxide, carbon dioxide, methane, nitrogen, and hydrogen sulfide at 1.03×10^5 Pa (0.25 psig) pressure and three different temperatures: 427, 593 and 816°C (800, 1100, and 1500°F). The ash sorbent, with 23 percent iron content, was the same as that used in fixed-bed experiments, with particle size ranging from -60 to +80 mesh. The space velocity was kept constant at 2297 h^{-1} and the inlet hydrogen sulfide concentration ranged between 1.00 and 1.25 percent. The test results showed an increase in ash absorption capacity after regeneration. The absorption capacity was 13 g H_2S/kg ash (92 grains H_2S/lb ash) at 371°C and 1.03×10^5 Pa, as compared to 8.6 g H_2S/kg ash (60 grains H_2S/lb ash) at 427°C and 1.53×10^5 Pa (80 psig) in the fixed-bed experiments. Some tests were also carried out by injecting carbonyl sulfide (0.1 - 0.17 percent), carbon disulfide (0.05-0.10 percent) and tars into the feed gases (25).

Further tests were conducted in fixed bed quartz and Iconel 601 reactors to determine the effect of operating parameters on the desulfurization process (28). Four gasifier ash sorbents with Fe_2O_3 contents ranging from 5 to 22 percent were used at Tyler Mesh particle sizes of 20x35, 10x20 and 4x8. The ash capacity was found to increase slightly with higher temperatures and increased number of cycles (A-8). The 4x8 size sorbent gave an efficiency of less than 65 percent at 15 percent breakthrough of H_2S, whereas smaller sizes had efficiencies of 80 to 90 percent in the temperature range of 538 to 760°C. It was found that the sorbents effectively removed COS and CS_2 as well as H_2S from simulated producer gases. However, the Inconel 601 was severely corroded by H_2S. Corrosion tests made on 1020 C.S., 304 S.S., 316 S.S., Incoloy 800, Inconel and Armco 18 SR showed that metals with low nickel content, such as Armco 18 SR, and chromium to nickel contents above 0.5 showed good corrosion resistance. Regeneration tests performed with air at 427-649°C gave O_2 efficiencies of 80-95 percent at 15 percent breakthrough. Two kinetic models were developed for the preliminary design of the commercial process.

- Uncertainties and Problems: In the cases of both the fixed and fluidized bed experiments, steam was not present in the inlet gases. The presence of steam would have had an adverse effect on desulfurization.

Regeneration with simultaneous sulfur extraction is not feasible, as discussed previously.

3.1.2.5 MERC Process: The Morgantown Energy Research Center (MERC) is investigating iron oxide (Fe_2O_3) supported sorbents for desulfurizing producer gases at 538-816°C (1000-1500°F). This research program was started in the late 1960's, and is still on-going. It was first funded by the U.S. Bureau of Mines, later by U.S. ERDA, and presently by the Department of Energy. Air Products and Chemicals, Inc. has assisted MERC in developing the desulfurization process.

The MERC process removes H_2S from raw producer gas at 538-816°C in fixed-bed absorbers containing Fe_2O_3 supported sorbents. The use of the support material reduces the attrition and loss of the Fe_2O_3 sorbent, one of the major problems which caused the shut-down of the Appleby-Frodingham Plant in England. In the absorber, H_2S

reacts with Fe_2O_3 to form FeS and FeS_2, with the empirical composition approaching $FeS_{1.5}$. The absorption reaction is mildly exothermic ($\Delta H = -91.3$ kJ/mole Fe_2O_3 or -21.8 kcal/mole Fe_2O_3). and can be shown as:

$$Fe_2O_3 + 3H_2S = 2FeS_{1.5} + 3H_2O.$$

This reaction can be obtained from the following two reactions, whose equilibrium constants are discussed under the IMMR Process:

$$Fe_2O_3 + 2H_2S + H_2 = 2FeS + 3H_2O$$
$$Fe_2O_3 + 4H_2S = 2FeS_2 + 3H_2O + H_2$$

Regeneration of the sorbent is achieved by passing a gas containing oxygen through the sulfided bed. The regeneration reactions is as follows:

$$2FeS_{1.5} + \frac{9}{2}O_2 \longrightarrow Fe_2O_3 + 3SO_2$$

This regeneration reaction is highly exothermic ($\Delta H = -1.466$ kJ/mole Fe_2O_3 or -350.1 kcal/mole Fe_2O_3). If during regeneration Fe_3O_4 is formed, excess oxygen in the regenerator converts the Fe_3O_4 to Fe_2O_3. The reactions are:

$$6FeS_{1.5} + 13O_2 \longrightarrow 2Fe_3O_4 + 9SO_2$$
$$2Fe_3O_4 + 1/2O_2 \longrightarrow 3Fe_2O_3$$

Another regeneration scheme which is being considered at MERC produces sulfur directly in the sulfided bed. According to this scheme, regeneration is simultaneously accomplished in two beds of sulfided sorbents. An oxygen containing gas, such as air, is supplied to the first bed, where the following reaction takes place:

$$4FeS + 7O_2 \longrightarrow 2Fe_2O_3 + 4SO_2$$

The SO_2 rich effluent gas from the first bed is then directed to the second bed, where the following reaction at 816°C produces sulfur:

$$3FeS + 2SO_2 = Fe_3O_4 + 5S$$

The Fe_3O_4 is then converted to Fe_2O_3 before returning to the absorption bed:

$$2Fe_3O_4 + 1/2O_2 \longrightarrow 3Fe_2O_3$$

Bench-scale tests (24,29,30,31) were intially carried out to screen absorbents for removing H_2S from producer gas at 538-816°C. These tests were conducted in a 25 mm I.D. stainless steel reactor tube with a simulated producer gas having the following composition: 5 percent CO_2, 26 percent CO, 1.5 percent H_2S, 17 percent H_2 and 50.5 percent N_2. The gas flow rate to the reactor was about 15 SCFH, and the space velocity was 2000 vol. gas/vol. bed/hr. Each absorption test was ended when the H_2S concentration from the reactor reached 0.15 percent (i.e., at 10 percent breakthrough). Forty-eight absorbents were tested. Among these, commercial catalysts, alkalyzed alumina, and taconite disintegrated; illmenite, open hearth slag, and blast furnace slag particles broke down and fused; sintered mixtures of 75 percent fly ash and 25 percent metal oxides (La_2O_3, Y_2O_3, CoO_3, SnO_2, ZnO) gave very low absorption capactities, pure sintered Fe_2O_3 showed acceptable absorption capacity, but disintegrated at 816°C. Pure fly ash had 25 percent of the absorption capacity obtained with a sintered mixture, 75 percent fly ash and 25 percent Fe_2O_3, but remained undamaged. The most promising absorbents were found to be sintered mixtures of 75 percent fly ash and 25 percent Fe_2O_3, 75 percent fly ash and 25 percent Jamaican red mud, 40 percent pumice and 60 percent Fe_2O_3, and pure red muds (Jamaican and Point Comfort).

Further investigations were performed to determine the optimum absorbent compositions. Sintered mixtures of fly ash and Fe_2O_3 containing more than 37 percent Fe_2O_3 showed pellet degradation. Sintered mixtures of 75 percent fly ash and 25 percent Fe_2O_3 and pure Jamaican red mud were found to have comparable absorption capacities. The 40 percent pumice and 60 percent Fe_2O_3 mixtures had similar absorption capacity as the fly ash Fe_2O_3 mixtures and pure red mud at 677°C (1250°F), but had lower absorption capacity at 816°C.

Absorbent durability was tested through six sulfiding-regeneration cycles. Regeneration was achieved with air at temperatures of 538-816°C. A reactor having a 63.5 mm I.D. was used to reduce the exposed reator wall surface per volume of gas. This change was made due to the reaction of H_2S with the reactor wall in the 25 mm I.D. reactor. Sintered red mud, pumice-Fe_2O_3 mixtures, and fly ash-Jamaican red mud mixtures suffered either pellet degradation or showed a tendency to fuse together. Sintered mixtures of 75 percent fly ash - 25 percent Fe_2O_3 did not exhibit any of these problems below 816°C, but fused at 871°C (1600°F). The fly ash-Fe_2O_3 sorbents were prepared by mixing 99 percent pure Fe_2O_3 powder, water and fly ash (-4 to +6 mesh) containing 47.9 percent SiO_2, 23.8 percent Al_2O_3, 15.7 percent Fe_2O_3, 0.6 percent P_2O_5, 2.8 percent TiO_2, 3.6 percent CaO, 1.5 percent MgO, 1.9 percent Na_2O and 2.2 percent K_2O. Pellets of about 6.35 mm diameter were formed, dried at 260°C (500°F), and finally sintered at 1093-1149°C (2000-2100°F) to increase their hardness.

Long-term absorption-regeneration tests were performed up to 174 cycles at temperatures of 538-816°C and a space velocity of 1000 vol. gas/vol. bed/hr. using sintered 75 percent fly ash and 25 percent Fe_2O_3. No reduction in absorption activity was observed in these tests with simulated dry and wet (containing 7 percent steam) producer gas. However, absorption capacity increased with temperature, and was found to be higher when the inlet gas did not contain steam. Figure 18 shows the relationship between temperature and absorption capacity. Tests with actual producer gases, which contained 8 g dust and 16 g tar per normal cubic meter (0.5 lb dust and 1 lb tar per 1000 SCF) of gas showed 95-97 percent H_2S removal. Some carbon deposition on the pellets, due to cracking of tars and accumulation of dust in the bed, was observed.

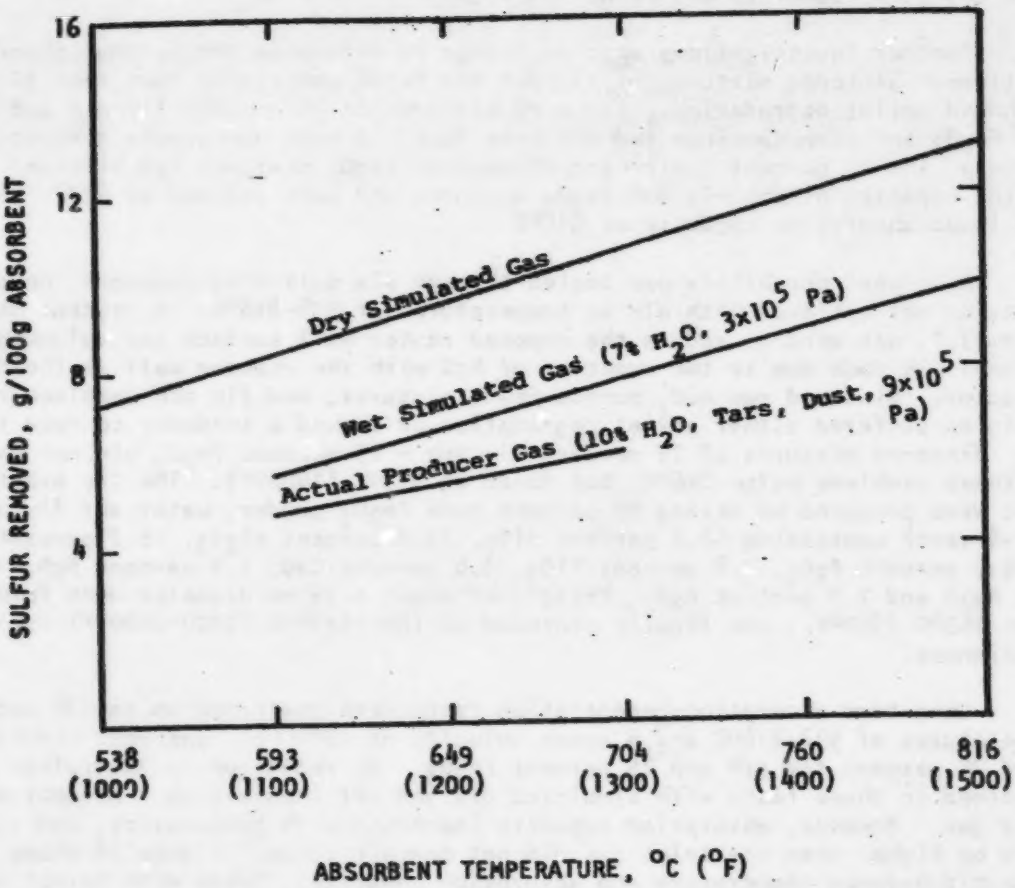


FIGURE 18. ABSORPTION CAPACITY OF SINTERED PELLETS OF 75% FLY ASH - 25% Fe_2O_3

Regeneration studies were conducted with both air and oxygen. With air at a space velocity of 1000 vol. gas/vol. bed/hr, the effluent SO_2 concentration reached about 10 percent. In the case of oxygen, more concentrated SO_2 effluents were obtained. In all cases, the bed temperature was kept below 816°C to avoid fusion of the pellets. Analysis of the sulfided sorbent indicated the empirical composition to be $FeS_{1.3}$. Figure 19 shows typical regeneration curves for air and/or oxygen.

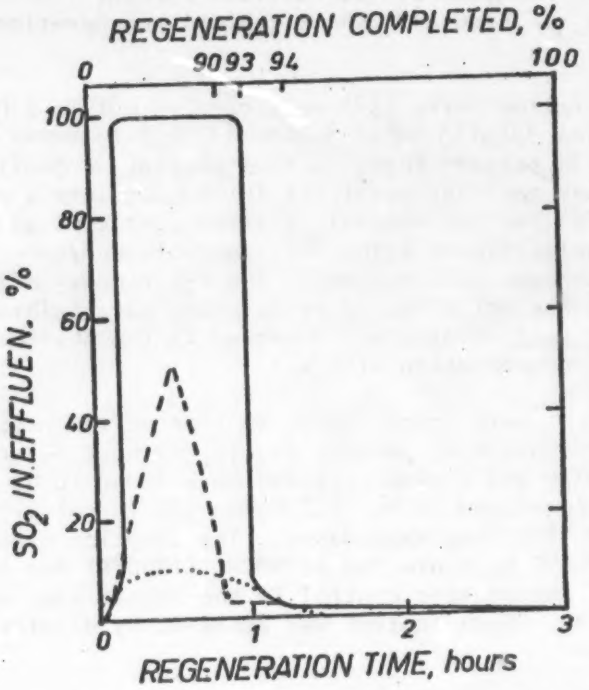
Further absorption tests (32) were carried out in a 15.2 cm(6") I.D. stainless steel reactor containing 33kg (73 lb) of 4.76mm (3/16") diameter sorbent pellets (75 percent fly ash - 25 percent Fe_2O_3, with 3 percent bentonite as binder). Low Btu gas from a fixed-bed gasifier was first introduced into a cyclone at a flow rate of 42.5 m^3 (1,500 SCFH) for the removal of large particles and then to the absorber at 593°C. The space velocity was 1,900 vol. gas/vol. bed/h. The absorption capacity of the sorbent averaged 8.25 percent. The H_2S removal efficiency was between 90 and 94 percent, and was not affected by tars and particulates in the inlet gas. However, deposition of particulates was observed in the absorber bed. These particles were burned out during regeneration with air.

Various binders were investigated to improve the physical strength of the sorbents (75 percent fly ash - 25 percent Fe_2O_3), without reducing the sorption capacity (33). Bentonite and sodium silicate were found to be satisfactory. The crushing strength was increased up to 31.8 kg/cm (70 lb/cm) with 12.7 mm (0.5") diamter and 9.65 mm (0.38") long extrudates. The sorption capacity was raised to 12-14 percent at 593-704°C by sintering at 982°C (1800°F) for 30 minutes in an oxidizing atmosphere. Temperature control in the regenerator was also studied to prolong the sorbent life. Such control was achieved by diluting the regenerator inlet air with nitrogen.

Mixtures of silica and Fe_2O_3 were also studied (34) since silica appeared to be superior to fly ash with respect to having more uniform properties and a higher melting point. Tests in the 50.8 mm I.D. absorber with 157 normal cm^3/s (20 SCFH) of simulated producer gas at temperatures around 982°C showed that mixtures of Fe_2O_3 and silica, containing up to 45 percent Fe_2O_3, are promising. The addition of sodium silicate was found to increase both sorption capacity and crush strength. A mixture of 55 percent silica and 45 percent Fe_2O_3, prepared with the addition of sodium silicate, had a crush strength of 30.9 kg/cm (68 lb/cm) and a capacity of 22.8 g H_2S/100 g sorbent.

Continous tests (35) were also performed in a larger-scale pilot plant. Flow rates up to 212 normal m^3/h (7500 SCFH) of coal gas were employed with absorbent containing 55 percent silica and 45 percent Fe_2O_3. Regeneration was accomplished with 5.7 normal m^3/h (200 SCFH) of air plus 42.5 normal m^3/h (1500 SCFH) of inert gas. Experimental difficulties were observed during six-day-long continuous testing.

Air Products and Chemicals, Inc. (APCI) provided assistance to MERC from early 1975 to 1977 (36,37,38). Under the APCI research program, sorbents were prepared by varying the source of iron oxide (7 sources), the iron oxide content of sorbents (from 8 to 63 percent), the support materials (fly ash and



—— Regeneration with O_2 (23.6cm^3/s, initial bed temperature of 454°C, maximum bed temperature of 732°C.)

---- Regeneration with Air (78.6 cm^3/s, initial bed temperature of 538°C, maximum bed temperature of 766°C.)

...... Regeneration with 50% Air - 50% O_2 Mixture (47.2 cm^3/s, initial bed temperature of 449°C, maximum bed temperature of 766°C.)

FIGURE 19. REGENERATION OF SULFIDED SORBENTS

silica), the type of binders (bentonite and kaolin), and the particle size of sorbents (3.18 and 6.35 mm diameter pellets). These sorbents were tested for such properties as crush strength, porosity, and surface area. They were evaluated after undergoing a single absorption and regeneration cycle. The recommended sorbents included 42 percent iron oxide on fly ash, 42 percent iron oxide on silica (for all sorption pressure ranges), and 63 percent iron oxide on fly ash (for sorption pressures around 400 psi). The 42 percent iron oxide sorbents had an absorption capacity around 0.18 sulfur/g absorbent, while the 63 percent iron oxide sorbent had absorption capacities of 0.13 gram sulfur/cm^3 absorbent at 20 psi and 0.32 g sulfur/cm^3 absorbent at 2.76×10^6 Pa (400 psi). Bentonite was found to be the preferred binder, and methocel was used as an extrusion aid. The effects of operating variables on the absorption and regeneration characteristics were also experimentally studied in the absorber. At a temperature of 649°C and a space velocity of 1800 vol. gas/vol. bed/hr, about 70 percent of the fresh absorbent capacity was utilized at the 10 percent breakthrough point (i.e., when the exit H_2S concentration reaches 10 percent of the inlet H_2S concentration). In the regenerator, with an inlet gas containing 85 percent steam and 15 percent air, 85 percent of the sorbed sulfur was removed after regeneration. Mathematical models were developed to fit the experimental absorption and regeneration data.

A review of the overall MERC project by DOE in 1977 resulted in a decision to suspend indefinitely the larger-scale process development work, and to emphasize supporting research (39). Under the revised program, the chemistry of hot gas clean-up was studied for more than 20 possible absorbents (46).

- Uncertainties and Problems: The exothermic regeneration reaction generates high temperatures, which can result in a loss of sorbent activity due to sintering. This problem was observed in the bench-scale tests while operating with both oxygen and air. Temperature control in the regenerator was better achieved by diluting air with nitrogen. However, this would reduce the SO_2 concentration in the regenerator effluent gas and increase the pumping cost and equipment size requirements due to the larger volumes of gases to be handled.

Corrosion of the stainless steel equipment was observed in the earlier tests. Suitable materials of construction need to be investigated.

Plugging of the control equipment occured in the large-scale continuous experiments. This problem might have occured due to the deposition of particulates as well as the condensation of tars at lower temperatures. Similar problems might also be expected in commercial scale operations.

3.1.3 HGC Processes Using Copper Based Absorbents

Four HGC processes using copper based absorbents have been identified. These include the Atlantic Refining -I, ESSO, Johns Hopkins and Kennecott Processes. None of these processes is currently being further developed. Among them, the most extensive testing was performed on the Johns Hopkins Process in the 1930's. Summarized information for these processes is presented below and in Table 6. Detailed information for these processes is presented in Sections 3.1.3.1 through 3.1.3.3.

TABLE 6 - HGC PROCESSES USING COPPER BASED SOLID ABSORBENTS

HGC PROCESSES	STATUS	ABSORBENT	ABSORPTION TEMP. (°C)	PRESSURE (Pa)	METHOD OF REGENERATION	REGENERATION TEMPERATURE (°C)	COMMENTS
Atlantic Refining -I	Terminated	Cu/Pb/Zn alumino-silicate	93- 538		steam Air	371- 538	
ESSO	Terminated	Supported Cu	299- 982		Cu_2O	399- 738	
Johns Hopkins	Terminated	Supported Cu/Cr/V	Up to 816		Air		Large Plant Tests
Kennecott	Terminated	Cu/CuO/ $Cu(OH)_2$	482 496	2×10^6 - 2.5×10^6	Air	816	

- Atlantic Refining Process -I : Heavy metal alumino-silicates such as copper aluminosilicate, lead aluminosilicate or zinc aluminosilicate, impregnated upon inert carriers, are used to desulfurize petroleum distillates and gases at temperatures between 93 and 530°C (200 and 1000°F). Regeneration of the spent sorbent is performed with steam and air at temperatures between 371 and 538°C (700 and 1000°F). Bench-scale experiments were conducted in the 1940's. There is no current research on this process.

- ESSO Process: Hydrogen sulfide from reducing gases is removed with copper containing solids at temperatures up to 982°C (1800°F) in a fluidized bed absorber. The cuprous sulfide is then reacted with cupric oxide at temperatures around 732°C (1350°F) to regenerate the copper and obtain sulfur dioxide gas. The cuprous oxide is produced by oxidizing copper in a separate vessel. Bench-scale experiments were carried out to test the different components and operations of the process. There is no current research on this process.

- Johns Hopkins Process: The Gas Engineering Department of Johns Hopkins University, supported by two gas companies, conducted extensive testing of copper, vanadium, chromium and uranium containing absorbents at temperatures up to 816°C (1500°F) to desulfurize coal gases. Laboratory pilot-scale, and large-scale plant tests were performed in the 1920's and 1930's. The research activities were terminated due to the unfavorable economic conditions during the depression and the increasing use of heavy oil.

- Kennecott Process: Hydrogen sulfide is absorbed by copper containing materials such as copper, copper hydrate, cupric oxide, and copper concentrate diluted with sand in proportions varying between 75 and 87.5 percent at temperatures between 482 and 496°C (900 and 925°F). Regeneration is with air at 816°C (1500°F). Bench-scale experiments were terminated in 1976 due to business related reasons.

3.1.3.1 Atlantic Refining Process—I : The Atlantic Refining Process -I , invented by Nachod, et al (41), was developed to desulfurize petroleum distillates and gases with heavy metal alumino-silicates at temperatures ranging from 93 and 538°C (200 to 1000°F). Regeneration of the spent sorbent is accomplished with steam and/or air at temperatures between 371 and 538°C (700 and 1000°F).

Impregnated treating materials such as metal salts or oxides, deposited upon inert carriers (e.g., clay), usually are subject to attrition, with the active material being separated from the carrier and removed with the gas to be desulfurized. This difficulty can be overcome by fixing the heavy metal ion (e.g., lead, copper, zinc) in such a way that it is still capable of effecting the desulfurizing reaction, yet is bound so tightly to the carrier that it cannot be removed, with resulting loss in capacity and contamination of the gas under treatment. This is accomplished by fixing the cation M in a cation exchanger AZ (such as sodium or potassium aluminosilicate) in the following manner:

$$AZ + M^{+} \longrightarrow MZ + A^{+}$$

The cation exchanger may first be formed by reacting sodium aluminate, sodium silicate and alum, in suitable proportions, in an aqueous solution at a pH between 3 and

9. The ratio of Na_2O to Al_2O_3 to SiO_2 may range from 1:1:2 to 1:1:8. The resulting alumino-silicate is then washed, dried, and treated with an aqueous solution of a heavy metal salt to replace the sodium with the heavy metal ions. The heavy metal alumino-silicate is washed and finally dried.

Lead and copper alumino-silicates were prepared by reacting sodium alumino-silicate and lead/copper acetate. The absorbents were then tested to remove sulfur compounds from vaporized naphtha at temperatures between 204 and 482°C (400 and 900°F) and a space velocity of 2 vol. naphtha/vol. alumino-silicate/hr. Sulfur compounds in the naphtha were reduced up to 43 percent.

There is no current work or future plans for further development of the process.

● Uncertainties and Problems: The available information on this process was obtained from a patent, which does not discuss any operating problems. Although the sorbent preparation method was described in the patent, and the use of some sorbents for hot gas desulfurization were experimentally demonstrated, the superiority of such prepared sorbents over impregnated materials was not proven.

The maximum sulfur removal efficiency reported in the patent was 43 percent. Such a low efficiency would only be useful for cleaning gaseous streams originating from low sulfur fuels.

The proposed regeneration methods were not experimentally demonstrated.

3.1.3.2 ESSO Process: The Esso Process, invented by Lewis (42), was developed to desulfurize reducing gases (such as coke oven gas, producer gas, water gas, hydrocarbon gases, and gases synthesized from petroleum oils) with copper-containing solids, and produce high quality sulfur dioxide gas from regeneration of the spent sorbent. No information could be obtained as to why the process was terminated. However, there is no current work or future plans to further develop this process.

The reducing gas fluidizes a bed of copper-containing solids at temperatures between 299 and 999°C(570 and 1830°F). The desulfurization reaction is:

$$2\,Cu + H_2S = Cu_2S + H_2. \qquad (1)$$

The variation of the equilibrium constant with temperatures for the above reaction is shown in Figure 20. As can be seen from Figure 20, hydrogen sulfide removal is thermodynamically favored at lower temperatures. However, rapid desulfurization is obtained at higher temperatures due to favorable kinetics.

Copper oxides are undesirable in the absorber since they undergo reduction with the incoming fuel gas by forming steam and carbon dioxide at the expense of hydrogen and carbon monoxide, thereby lowering the heating value of the desulfurized gas. On the other hand, when the sorbent is copper rather than the copper oxides, removal of hydrogen sulfide takes place with simultaneous generation of hydrogen.

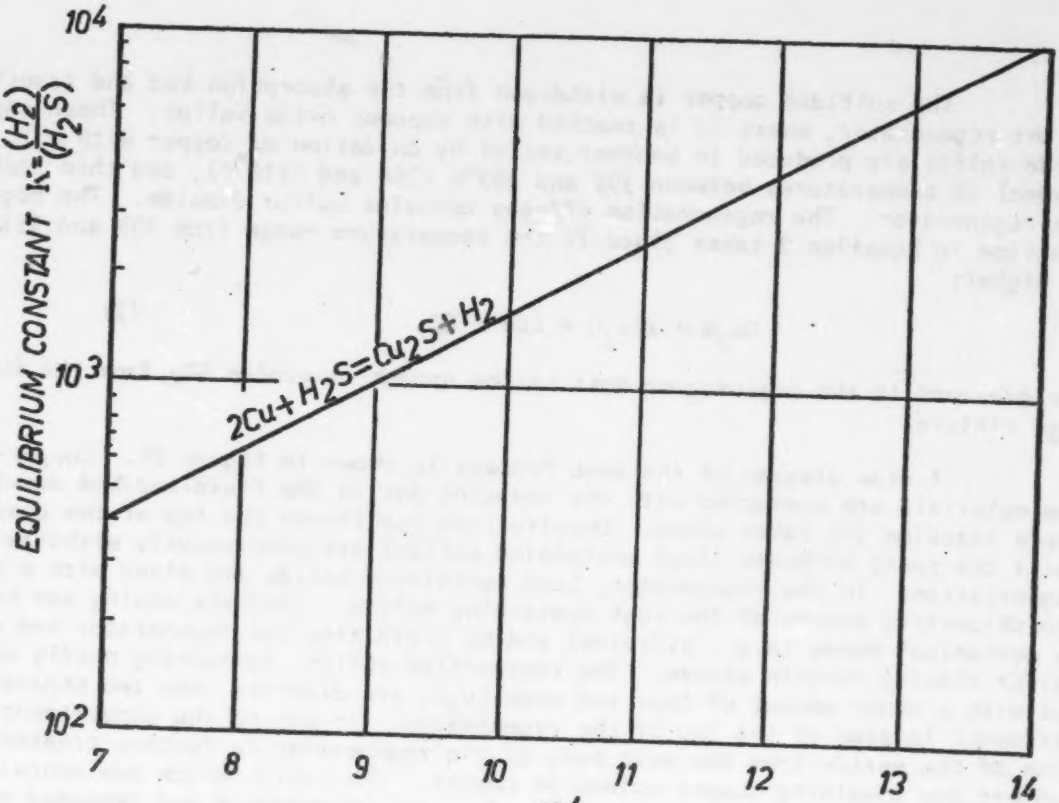


FIGURE 20. EQUILIBRIUM CONSTANT FOR THE REACTION:
$2Cu + H_2S = Cu_2S + H_2$

The sulfided copper is withdrawn from the absorption bed and transferred to the regenerator, where it is reacted with cuprous oxide solids. These cuprous oxide solids are produced in another vessel by oxidation of copper with air (or oxygen) at temperatures between 399 and 593°C (750 and 1110°F), and then passed to the regenerator. The regeneration off-gas contains sulfur dioxide. The regeneration reaction in Equation 2 takes place in the temperature range from 399 and 593°C, or higher:

$$Cu_2S + 2Cu_2O = 6Cu + SO_2. \qquad (2)$$

The pressure in the regenerator must be low enough to evolve SO_2 from the Cu_2S - Cu_2O mixture.

A flow diagram of the Esso Process is shown in Figure 21. Copper-containing materials are contacted with the reducing gas in the fluidized-bed desulfurizer, where reaction (1) takes place. Desulfurized gas leaves the top of the absorber, while the spent sorbents (Cu_2S containing solids) are continuously withdrawn for regeneration. In the regenerator, Cu_2O containing solids are mixed with a small stoichiometric excess of the Cu_2S containing solids. Intimate mixing can be obtained by mechanical means (e.g., stirring) and by fluidizing the regenerator bed with a sulfur dioxide recycle stream. The regenerated solids, containing mostly copper, but with a minor amount of Cu_2S and some Cu_2O, are directed into two separate compartments located at the top of the regenerator. In one of the compartments, a portion of the solids from the main body of the regenerator is further treated to convert any remaining copper oxides to copper. The solids which now contain mostly copper and some Cu_2S are then withdrawn from the regenerator and returned to the desulfurizer. In the other compartment, a portion of the regenerated solids is exposed to an excess of Cu_2O from the oxidizer, thereby ensuring that the solids drawn off from this compartment into the oxidizer are practically free of Cu_2S. A portion of the regenerator effluent gas is recycled to the regenerator as a fluidizing agent.

In the oxidizer, air or oxygen-containing gas is reacted with Cu to form Cu_2O according to the following reaction:

$$2Cu + 1/2O_2 = Cu_2O \qquad (3)$$

The Cu_2O solids from the oxidizer are returned to the regenerator for reaction with Cu_2S.

Bench-scale experiments were performed to test the desulfurization and regeneration reactions. Copper-containing solids were prepared by impregnating silica gel with a copper nitrate solution. The mix was then dried, roasted in air, crushed to sizes finer than 100 mesh, and reduced with hydrogen at a temperature of 149 to 204°C (300 to 400°F). A hydrogen gas stream, with 1.0 - 1.5 percent H_2S, was contacted with copper impregnated silica gel containing 2 to 20 percent Cu. Flow rates greater than 3.12 cm^3/s/g Cu (180 SCFH gas/lb Cu) in the bed were employed. Space velocities were greater than 500 vol gas/vol.bed/h . Hydrogen sulfide removal was determined at different temperatures. Within the optimum temperature

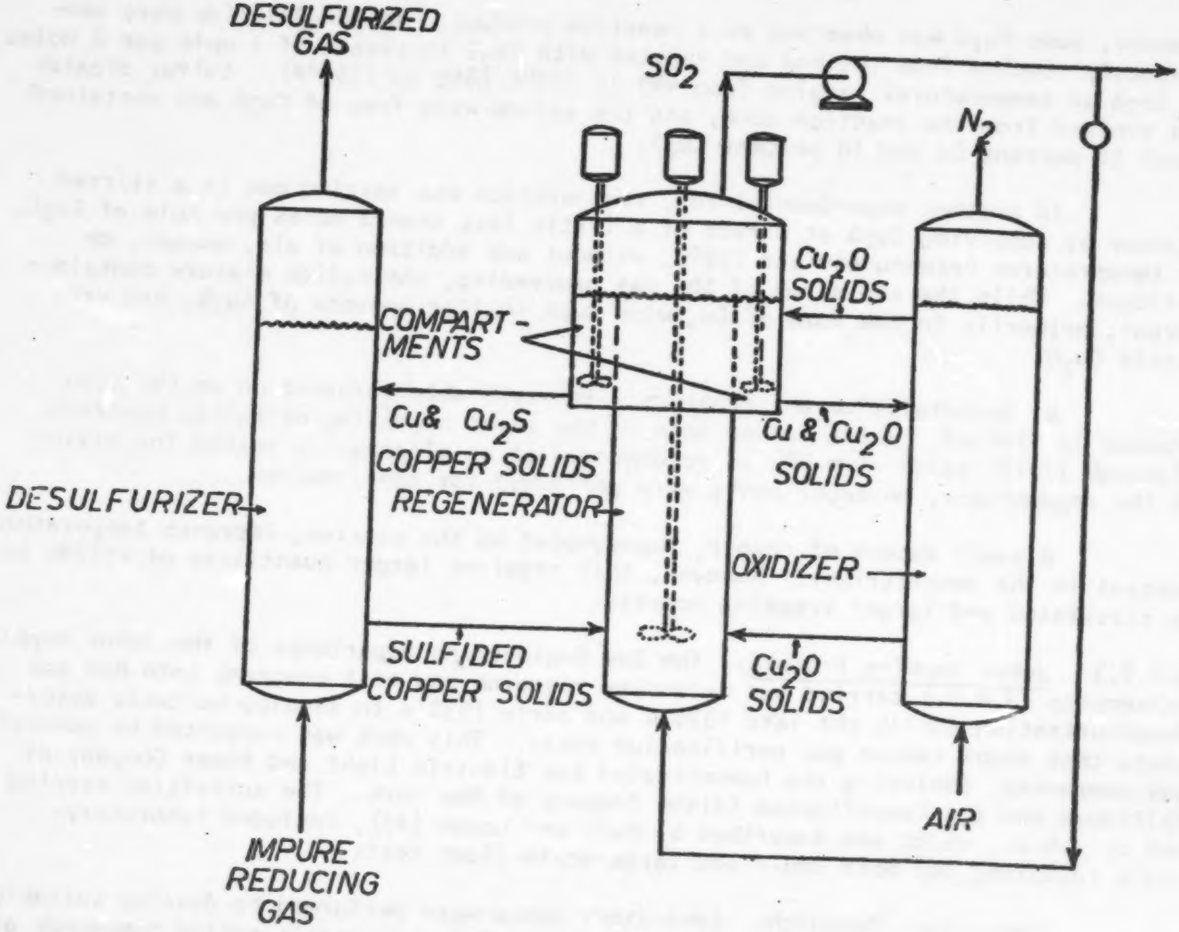

DESULFURIZED GAS
SO$_2$
N$_2$
Cu$_2$O SOLIDS
COMPARTMENTS
Cu & Cu$_2$S COPPER SOLIDS
Cu & Cu$_2$O SOLIDS
DESULFURIZER
REGENERATOR
OXIDIZER
SULFIDED COPPER SOLIDS
Cu$_2$O SOLIDS
AIR
IMPURE REDUCING GAS

FIGURE 21. ESSO PROCESS

range of 349 to 593°C (660 to 1110°F), the removal efficiency was about 98.5 percent. At higher temperatures, in the range of 593 to 927°C (1100 to 1700°F), the removal efficiency was found to be between 80 and 95 percent.

Regeneration of the spent sorbent was first accomplished in a bed fluidized with air at temperatures between 399 and 704°C. The air rate was controlled to provide only enough oxygen to convert the Cu_2S to Cu by the reaction:

$$Cu_2S + O_2 = 2Cu + SO_2 \qquad (4)$$

However, some Cu_2O was observed as a reaction product. The Cu_2O solids were continuously removed from the bed and reacted with Cu_2S in excess of 1 mole per 2 moles of Cu_2O at temperatures ranging from 449 to 738°C (840 to 1360°F). Sulfur dioxide gas evolved from the reaction zone, and the solids were free of Cu_2O and contained about 90 percent Cu and 10 percent Cu_2S.

In another experimental run, regeneration was carried out in a stirred reactor by supplying Cu_2O at a rate of a little less than 2 moles per mole of Cu_2S, at temperatures between 449 and 738°C, without any addition of air, oxygen, or nitrogen. While the evolution of SO_2 was proceeding, the solids mixture contained copper, primarily in the form of Cu, with much smaller amounts of Cu_2S, and very little Cu_2O.

- Uncertainties and Problems: The available information on the Esso Process is limited. There are no data on the level of mixing or solids handling. Although fluidization with SO_2 is recommended as an alternative method for mixing in the regenerator, no experiments were performed for confirmation.

A small amount of copper, impregnated on the carrier, improves temperature control in the desulfurizer. However, this requires larger quantities of solids to be circulated and larger treating vessels.

3.1.3.3 Johns Hopkins Process: The Gas Engineering Department of the Johns Hopkins University (J.H.U.) carried out extensive research and test programs into hot gas desulfurization during the late 1920's and early 1930's to develop suitable absorbents that might reduce gas purification costs. This work was supported by several gas companies, including the Consolidated Gas Electric Light and Power Company of Baltimore and the Consolidated Edison Company of New York. The activities carried out by J.H.U., which are described by Huff and Logan (43), included laboratory-scale research, and both small and large-scale plant tests.

Laboratory Research: Laboratory tests were performed to develop suitable absorbents for the simultaneous removal of both H_2S and organic sulfur compounds at elevated temperatures. Blue gas, containing about 2.29 grams of H_2S and 0.09-0.18g of organic sulfur per m^3 of gas, (100 grains of H_2S and 4-8 grains of organic sulfur per 100 ft^3 of gas) was used for test purposes. Regeneration on the sulfided absorbent was achieved by blowing air through the sulfided absorbent at a flow rate of 15.7 cm^3/s (2 ft^3/h). The first experiments made on copper oxide and iron oxide showed that neither copper nor iron alone was effective for removing sulfur. Copper did not absorb sulfur at 349 and 449°C (660 and 840°F), whereas iron oxide plugged quickly with carbon at 449°C, and could not be regenerated at 349°C. Other absorbents tested in the range of 249 and 449°C (480 to 840°F) with commercial blue gas included 85 percent copper - 15 percent uranium on pumice, 50 percent copper - 50 percent uranium, 80 percent copper - 10 percent uranium - 10 percent chromium, 80 percent tin - 20 percent uranium, 60 percent tin - 40 percent uranium, 80 percent antimony - 20 percent uranium, 80 percent uranium - 20 percent cerium, 80 percent bismuth - 20 percent uranium on pumice, compressed lime, compressed molybdenum, 85 percent iron - 10 percent uranium - 5 percent manganese, and compressed vanadium. Of these materials, the copper-uranium-chromium mixture gave the most promising results.

Next, continuous tests were carried out at 450°C (842°F) with 15 cm^3 of absorbent consisting of 80 percent copper, 10 percent uranium and 10 percent chromium. Blue gas, with the following composition, was used in these tests: 13.2 percent CO_2, 2.1 percent O_2, 14.9 percent H_2, 16 percent CO, 0.1 percent CH_4, 0.2 percent C_2H_6, and 53.5 percent N_2. The amounts of H_2S and organic sulfur added to 1 m^3 of this gas were 1.56-3.09 and 0.09-0.18 grams (78-135 grains H_2S/100 ft^3 gas and 4-8 grains organic sulfur/100 ft^3 gas), respectively. The space velocity was approximately 3,000 per hour. About 0.03 m^3 of air was used to regenerate the absorbent. Hydrogen sulfide removal was above 97.3 percent in all cases. The addition of 30 percent steam to the inlet gas improved the efficiency of hydrogen sulfide removal to over 99 percent and resulted in almost complete removal of organic sulfur.

While the mechanism of the reactions was not investigated, Huff and Logan concluded that uranium or chromium is primarily responsible for the conversion of organic sulfur to hydrogen sulfide, and copper for the absorption of sulfur as hydrogen sulfide.

Additional tests were made to develop a suitable carrier or binder for the active material, to enable it to withstand plant use without crumbling. These tests included such treatments as fusing the active material (copper, vanadium, chromium, uranium) either alone or with aluminum, and baking with alundum cement or clay. These tests indicated that copper-vanadium-clay mixtures were the most promising. A mixture of 70 percent clay - 30 percent oxides (80 percent copper - 20 percent vanadium as metals), baked at 899-949°C (1650-1740°F), removed hydrogen sulfide and organic sulfur completely from a carburetted water gas containing 1.97 to 20.0 g H_2S/m^3 (86 to 875 grains H_2S/100 ft^3) gas at 449°C. The absorption-regeneration cycle consisted of 3.5 minutes for absorption, followed by 3 minutes for regeneration. The space velocity was about 5,600 per hour.

Small-Scale Plant Tests: On the basis of the encouraging laboratory tests described above, a test apparatus was installed in 1928 at the Spring Gardens Plant of the Consolidated Gas Electric Light and Power Company of Baltimore. This apparatus was attached to the top of a superheater for backrun carburetted water gas produced by a water gas machine, and heated independently to maintain the desired experimental temperatures. The operating conditions were more adverse than those prevailing in the laboratory, especially with respect to the presence of dust and tar in the raw carburetted water gas. The ability to control the temperature of the purification process, and the concentration of the oxygen in the blast gas during regeneration, were maintained during these tests.

An absorbent of 80 percent copper - 20 percent vanadium mixed with clay (70 percent clay and 30 percent oxides) was molded into small rings (1.45 mm long x 13.5 mm O.D. x 7.1 mm I.D.), and tested at temperatures between 482 and 510°C. In one experiment of 33.5 hours duration, 7.96 m^3 (281 ft^3) of gas containing 2.47g H_2S/m^3 (108 grains $H_2S/100\ ft^3$) was completely desulfurized with 0.64 lb of purifying material. Regeneration was achieved by means of air.

These promising results led to the installation of a similar, but larger, apparatus operating on both uprun and backrun gas which contained 3.00 and 5.1 g H_2S/m^3 (131 and 222 grains $H_2S/100\ ft^3$), respectively, and about 0.39 g organic sulfur/m^3 (17 grains organic sulfur/100 ft^3). Average removal efficiencies of 93.2 percent for H_2S and 74 percent for organic sulfur were obtained. Short tests also indicated copper-chromium-clay mixtures to be promising.

Small plant tests were continued in an attempt to reduce the cost of producing the absorbent by coating clay forms with a layer composed of 60 percent clay and 40 percent oxides.

In a 1500 hour experiment conducted at around 538°C, hydrogen sulfide removal efficiency was 79.5 percent during the first 200 hours and 66.7 percent during the last 200 hours. Removal of organic sulfur averaged about 65 percent. The space velocity in this experiment was 2,000 per hour. The gas flow varied between 8.1 to 10.2 m^3/hr (282 to 360 ft^3/hr), and H_2S concentration in the inlet gas was between 2.4 and 3.4 g/m^3 (106 and 147 grains/100 ft^3). Another experiment was conducted to determine the effect of increased temperature. Raising the temperature from 510°C to above 816°C, and then lowering it to 527°C, did not affect the activity of the material and the removal of hydrogen sulfide remained in the neighborhood of 85 percent.

Large-Scale Plant Tests: Large-scale plant tests were performed by placing the coated absorbent forms in the top of a superheater, instead of placing them in a separate chamber outside the superheater, to save the cost of additional plant equipment.

The first test was carried out at the gas plant in Baltimore discussed previously. Nine thousand small, circular, finned forms (with copper-vanadium mixtures as active material) were used, occupying a space of about 1.82 m in diameter and 0.91 m in height. This test lasted 442 hours, during which the removal efficiency decreased from 76.4 percent to 41 percent. The number of forms was then increased to 23,000 for the next test. However, an initial desulfurization efficiency of 75-80 percent declined to 24 percent after 3,700 hours of operation. Regeneration was achieved by introducing air at the bottom of the superheater.

Two additional plant-scale experimental programs, one in Baltimore and the other in New York, were intiated during 1930. Results were generally similar to the initial tests, with absorbent activity decreasing dramatically with time. The facility at the Central Union Plant of the Consolidated Edison Company in New York was first run with 2,100 forms of the kind used previously in the test in Baltimore. These forms occupied the upper third of the superheater. The removal efficiency dropped from 49.5 to 39 percent after 1300 hours of operation. The number of forms was then increased to 60,000 and an efficiency of 77.5 percent was obtained with carburetted water gas for the first 100 hours. However, the efficiency dropped to 67 percent after about 800 hours of operation, and then to below 50 percent. Laboratory tests showed a loss of active chemicals, particularly copper, from the absorbent coatings.

Tests at Baltimore were performed with coated rectangular grid forms, employing copper-vanadium as the active material. An initial efficiency of 91 percent for the first 600 hours dropped to about 20 percent after 2,200 hours of operation. Loss of active material was also experienced during these tests.

The large-scale plant tests gave lower removal efficiencies than the earlier laboratory and small-scale plant tests. This was due to the high temperatures (about 760-816°C in the superheaters, as compared to 538°C in small-scale tests), the presence of excessive chloride impurities, high ash, and frequent leaching with steam when treating the raw carburetted water gas.

Investigation of the lowering of activity of the coated forms led to the development of a modified form in which the active chemicals, copper and chromium, were heavily incorporated throughout the material.

The formula was 55 parts clay, 20 parts stoneware grog,, and 25 parts oxides (18.87 Cu_2O, 6.13 Cr_2O_3). Tests performed at Spring Gardens, Baltimore, showed removal efficiencies of 60.7 percent the first month and 15 percent at the end of 7800 hours of testing. As was the case with the coated forms, considerable loss of copper was again experienced.

Laboratory tests suggested that the loss of activity might be due to a slow chemical reaction between the copper and the silica of the clay. Preliminary tests were carried out to develop an absorbent that would maintin its activity during plant use. Studies were made to determine the effects of adding an alkaline (MgO) substance to the absorbent mixture. While preliminary results were encouraging, no plant data was obtained with the new absorbent forms because research activites were suspended. The apparent reasons for terminating this test program involve the economic conditions during the period of "the depression", and the increasing use of heavy oil during the 1930's, which obviated the need for coal-derived water gas.

Problems experienced at the various stages of development of the Johns Hopkins Process are incorporated in the discussions pertinent to each stage.

3.1.3.4 Kennecott Process: Kennecott Copper Corporation (KCC) investigated the applicability of copper-containing absorbents for hot gas desulfurization. Research at the Ledgemont Laboratory of KCC started in 1971, and was terminated in 1976 due to business related reasons. The research program was internally funded (A-9).

Bench-scale experiments were carried out in a reactor of 25 mm I.D. and 15 cm height (A-10). Operation with Lurgi fuel gas at 2.0×10^6 - 2.5×10^6 Pa (20-25 atm) pressure was simulated by using bottled gases with the equivalent hydrogen sulfide partial pressure at 1.0x10^5Pa (1 atm) total pressure (47). The inlet bottle-gas composition was: 23 percent H_2S, 30 percent CO, and 47 percent H_2. Four different copper containing absorbents were tested: copper metal (Cu), copper hydrate ($Cu(OH)_2$), cupric oxide (CuO) and copper concentrate (24.3 percent Cu, 26 percent S, 21.5 percent Fe). These absorbents were diluted with sand in proportions varying between 75 percent and 87.5 percent of sand (by weight). Successive absorption and regeneration cycles (3 or 4 cycles per experiment) were conducted at absorption temperatures of 482 and 510°C (900 and 950°F) and a regeneration temperature of 816°C (1500°F). Each of the four absorbents was found to be capable of removing in excess of 90 percent of the hydrogen sulfide, with a gas residence time of about 0.5 seconds. Each of the sulfided absorbents was regenerated with air at 816°C with a similar reaction time. The regeneration off-gas contained 12-14 percent sulfur dioxide for 99 percent regeneration of the sulfided absorbent.

The equilibrium constants for reactions involved in the absorption cycle are given in Figure 22 as a function of temperature. This figure indicates that cuprous sulfide is the absorption product, even when cupric oxide is used as an absorbent under reducing atmosphere.

- Uncertainties and Problems: The scale of these tests was too small to draw any definite conclusions regarding the technical or economic feasibility of the process.

Hot gas desulfurization was studied over the temperature range between 482 and 510°C. No testing was performed beyond this range. Regeneration tests were not conducted at any other temperature but 816°C.

The simulated fuel gas contained only hydrogen sulfide, carbon monoxide and hydrogen. However, the presence of carbon dioxide and steam would reduce the sulfur removal efficiency. Also, the presence of particulates and tars in the fuel gas might cause operational problems.

Removal of carbonyl sulfide and any other organic sulfur was not demonstrated experimentally.

An initial period of incomplete hydrogen sulfide absorption was observed for all the absorbents tested. This might be due to the evolution of sulfur dioxide resulting from the reduction of copper sulfate formed in the regeneration cycle.

The temperature difference between absorption and regeneration steps is more than 260°C (500°F). This would reduce the overall efficiency of the process. The absorption reactions are thermodynamically favored at lower temperatures, whereas the regeneration reaction is favored at higher temperatures. Regeneration at low temperatures results in the formation of copper sulfate.

3.1.4 HGC Processes Using Zinc Based Solid Absorbents

Three HGC processes using zinc based solid absorbents were identified, including the Atlantic Refining -I , Catalysts and Chemicals, and IFP Processes.

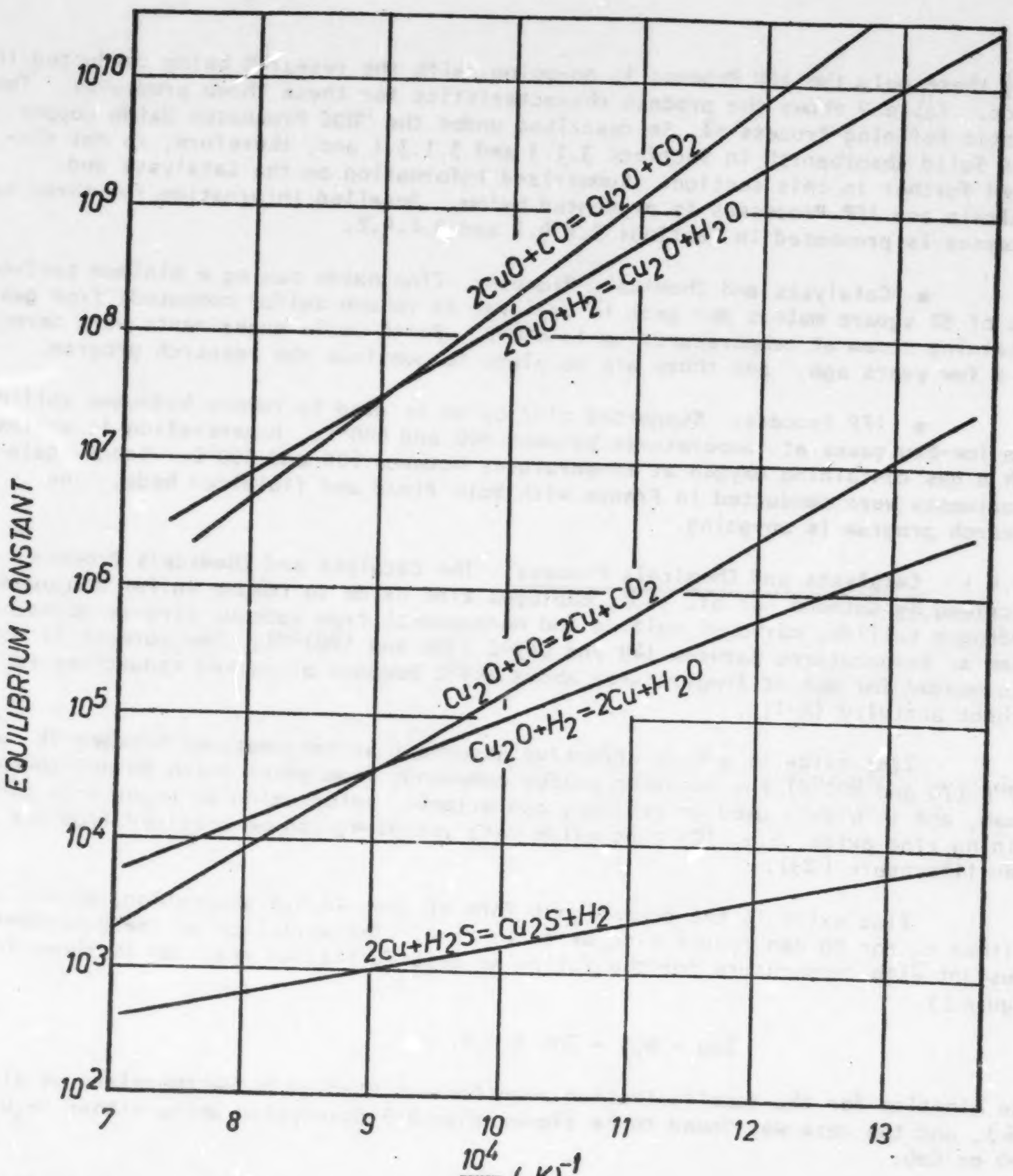


FIGURE 22. EQUILIBRIUM CONSTANTS FOR DESULFURIZATION WITH COPPER-CONTAINING ABSORBENTS

Among these only the IFP Process is on-going, with the research being conducted in France. Table 7 shows the process characteristics for these three processes. The Atlantic Refining Process -I is described under the "HGC Processes Using Copper Based Solid Absorbents" in Sections 3.1.3 and 3.1.3.1 and, therefore, is not discussed further in this section. Summarized information on the Catalysts and Chemicals and IFP Processes is presented below. Detailed information for these two processes is presented in Sections 3.1.4.1 and 3.1.4.2.

- Catalysts and Chemicals Process: Zinc oxide having a minimum surface area of 30 square meters per gram is employed to remove sulfur compounds from gases containing steam at temperatures up to 650°C. Bench-scale experiments were terminated a few years ago, and there are no plans to continue the research program.

- IFP Process: Supported zinc oxide is used to remove hydrogen sulfide from low-Btu gases at temperatures between 400 and 600°C. Regeneration is achieved with a gas containing oxygen at temperatures between 600 and 900°C. Bench-scale experiments were conducted in France with both fixed and fluidized beds. The research program is on-going.

3.1.4.1 Catalysts and Chemicals Process: The Catalyst and Chemicals Process described by Gutmann, et al. (45), employes zinc oxide to remove sulfur compounds (hydrogen sulfide, carbonyl sulfide and mercaptans) from gaseous streams containing steam at temperatures between 149 and 649°C (300 and 1200°F). The sorbent is not recommended for use at temperatures above 649°C because of marked reductions in sorbent activity (A-11).

Zinc oxide is a very effective absorbent at temperatures between 21 and 427°C (70 and 800°F) for removing sulfur compounds from gases which do not contain steam, and is widely used in refinery operations. Information on absorbents containing zinc oxide, e.g. ICI zinc oxide catalyst 32-4, can be obtained from the open literature (23).

Zinc oxide is the predominant form of zinc in H_2S absorption, mainly since neither H_2 nor CO can reduce zinc oxide to zinc. The variation of the equilibrium constant with temperature for the following desulfurization reaction is shown in Figure 23.

$$ZnO + H_2S = ZnS + H_2O.$$

The kinetics for the desulfurization reaction was studied by Westmoreland et al. (46), and the rate was found to be slower than H_2S absorption using either Fe_2O_3, MnO or CaO.

The presence of steam in gas streams reduces the effectiveness of the zinc oxide and, for this reason, zinc oxide has not been recommended for treatment of such streams. However, Gutmann, et al., found that at temperatures above 148°C (300°F), there is a direct relationship between the surface area of zinc oxide and its affinity for sulfur compounds in gaseous streams containing steam. The recommended surface area of zinc oxide is generally between 30 and 100 square meters

TABLE 7 - HGC PROCESSES USING ZINC BASED SOLID ABSORBENTS

HGC PROCESSES	STATUS	ABSORBENT	ABSORPTION TEMP. (°C)	PRESSURE (Pa)	METHOD OF REGENERATION	REGENERATION TEMPERATURE (°C)	COMMENTS
Atlantic Refining -I	Terminated	Zn/Cu/Pb Aluminosilicate	93 - 538		H_2O Air	370 - 538	
Catalysts & Chemicals	Terminated	ZnO	150-650	6×10^5-2.6×10^6			Regeneration not studied
IFP	On-Going	Supported ZnO	400-600		O_2 Containing Gas	600-900	Proprietary process

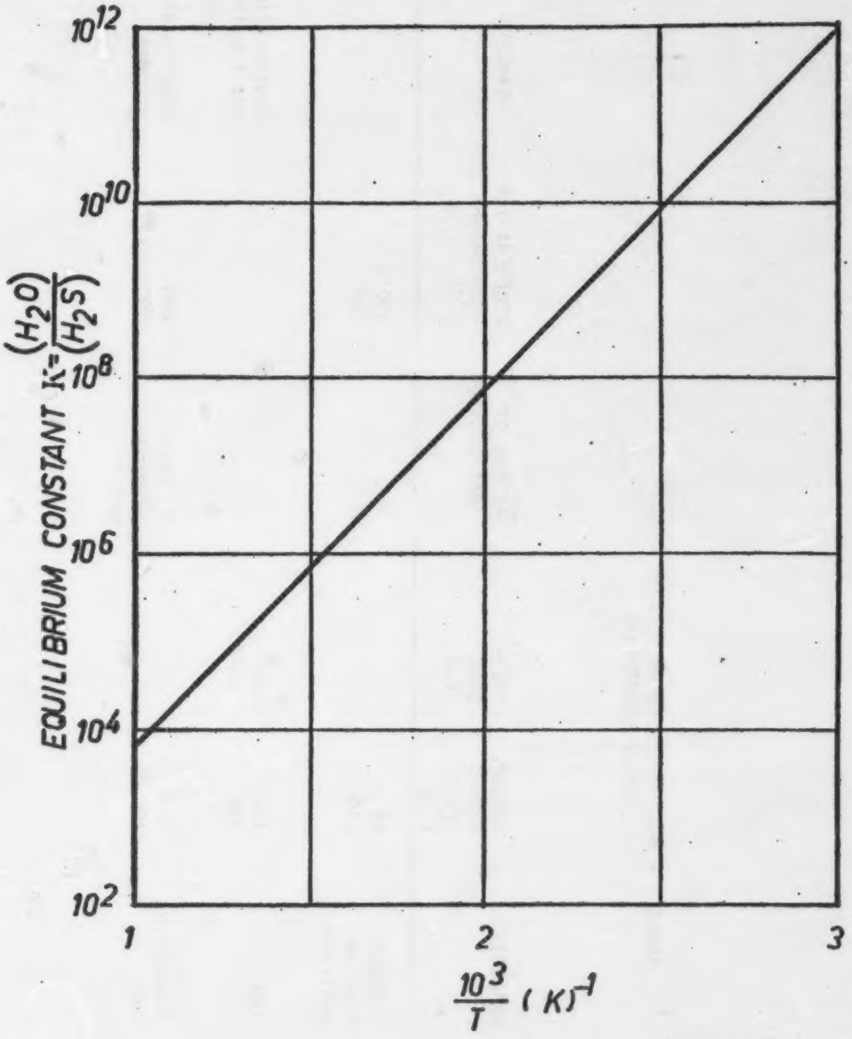


FIGURE 23. EQUILIBRIUM DATA FOR THE REACTION:
$ZnO + H_2S = ZnS + H_2O$

per gram. In the case of effluent streams from steam reforming or from the first stage of shift conversion processes, and area between 30 and 60 square meters per gram is recommended.

A set of bench-scale absorption experiments (45) were performed by passing a "dry" gas stream containing 99.7 percent nitrogen and 0.3 percent hydrogen sulfide through a fixed bed containing 48 mm ZnO pellets and extrudates at a temperature of 400°C and 7.8×10^5 Pa (100 psig) pressure. The sorbent capacities were 15 percent and 18.2 percent when the surface areas of zinc oxide were 5 and 30-40 square meters per gram, respectively. These experiments show that, in removing hydrogen sulfide from a gas stream which contains no steam, there is little difference in the capacity of high and low surface area zinc oxide for hydrogen sulfide.

Another set of absorption experiments was conducted with a gas mixture containing 3.5 percent carbon monoxide, 22.5 percent carbon dioxide, 55.0 percent hydrogen, and 19.0 percent nitrogen at 232°C (450°F) and 2.8×10^6 Pa (400 psig) pressure. The hydrogen sulfide concentration in the inlet gas was 50 ppm, and the steam to gas ratio 0.6. Sorbent capacity was 1 percent at 9 square meters per gram of zinc oxide, and 6 percent at 30 square meters per gram of zinc oxide. These experiments show that when steam is present in the gas stream, the affinity of zinc oxide for sulfur compounds is increased when higher surface area zinc oxides are employed.

Regeneration of the sulfided sorbent was not attempted. Further experiments were also carried out to remove carbonyl sulfide (COS) with zinc oxide. However, the tests results are not available.

- Uncertainties and Problems: The information concerning the Catalyst and Chemicals Process is limited, and the experimental difficulties are not discussed in the patent. However, it is known that the process is restricted to the removal of "trace" quantities of hydrogen sulfide, due to process economics. For the same reason, regeneration of the sulfided absrobent is not feasible. Operation below 649°C (1200°F) is recommended to prevent the loss of activity of the sorbent.

3.1.4.2 IFP Process: Institut Français du Pétrole (IFP) is developing a process using supported zinc oxide (ZnO) for the desulfurization of low-Btu gases at temperatures between 400 and 600°C (A-12).

Laboratory tests were performed by passing a synthetic low-Btu gas through both fixed and fluidized beds containing 100 grams of absorbent in an electrically heated quartz reactor. In the fixed bed experiments, various metal oxides were tested, and zinc oxide was found to be active as well as thermally stable. The chemistry of the absorption reaction is discussed under the Catalyst and Chemicals Process.

In fixed bed runs of about 100 cycles each, the optimum operating conditions—based upon desulfurization efficiency, absorption capacity and absorbed life— were obtained at temperatures between 400 and 600°C. Regeneration of the sulfided sorbent was achieved with a gas containing oxygen. A low regeneration temperature favored the formation of zinc sulfate, which resulted in the emission of SO_2 in the subsequent absorption cycle, whereas a high regeneration temperature reduced the absorbent capacity due to crumbling of the bed particles. The temperature rise in the regenerator was controlled by limiting the oxygen concentration in the inlet gas.

Fluidized bed experiments were also carried out with a synthetic low-Btu gas containing 1 percent H_2S, at desulfurization temperatures of 400-600°C. The sorbent particles were 0.3-0.5 mm in diameter and contained 70 percent zinc oxide by weight. The sulfided sorbent was regenerated with a gas containing 4 percent oxygen at temperatures between 600 and 900°C. Table 9 shows the results of a run which lasted 2200 hours, during which the sorbent was cycled 615 times.

TABLE 8. FLUIDIZED BED ABSORPTION-REGENERATION EXPERIMENT

Cycle No.	Sorbent Capacity for H_2S exit conc. $\leq$ 500 ppm (mol H_2S/kg Sorbent)	$H_2S + SO_2$ Conc. from Absorber (ppm)
1	7	70
50	3.5	90
200	2.2	100
600	2	140

- Uncertainties and Problems: The available information on the IFP Process is very limited. This process seems to be at an early stage of development. There is no information on the nature of the support material. The use of low-Btu gas containing tars might severely effect the sorbent characteristics.

3.1.5 HGC Processes Using Other Solid Absorbents

The processes described in this section are those which could not be included in the categories of solid absorbents discussed in Sections 3.1.1 through 3.1.4. Two such processes, consisting of the Exxon and Foster Wheeler Processes, have both been terminated. There is no indication for further development. Table 9 presents the process characteristics of these two processes. Summarized information is presented below, while Sections 3.1.5.1 and 3.1.5.2 provide more detailed discussions.

- EXXON Process: Lanthanum oxide deposited on steam-treated and calcined alumina removes hydrogen sulfide at temperatures and pressures up to 927°C (1700°F) and 7.8×10^5 Pa (100 psig). Regeneration at these conditions is achieved by treating the sulfided sorbent first with steam and then with an oxidizing gas. Bench-scale work at Exxon Research and Engineering Company was terminated in the early 1970's.

- Foster Wheeler Process: Hydrogen sulfide from coal gases is removed with nickel containing absorbents at temperatures between 538 and 788°C (1000 and 1450°F). The sulfided sorbent is regenerated with air at temperatures between 538 and 732°C (1000 and 1350°F). Bench-scale experiments were terminated in 1976 in favor of higher priority projects.

TABLE 9 - HGC PROCESSES USING OTHER SOLID ABSORBENTS

HGC PROCESSES	STATUS	ABSORBENT	ABSORPTION TEMP. (°C)	PRESSURE (Pa)	GAS FLOW RATE normal m^3/h	METHOD OF REGENERATION (°C)	REGENERATION TEMPERATURE
Exxon	Terminated	Supported La_2O_3	149-927	1×10^5-6×10^5		Steam Air/O_2	149-927
Foster Wheeler	Terminated	Supported Ni	538-788		0.10	Air	538-788

3.1.5.1 Exxon Process: The Exxon Process, invented by Wheelock, et al. (47), removes hydrogen sulfide and organic sulfur by means of a rare earth metal component deposited on steam-treated and calcined alumina at elevated temperatures. This process was developed as an improvement over an earlier process (48) that employed unsteamed support material. Suitable rare earth metal components include metals having an atomic number 57 through 71 inclusive, or mixtures thereof. The preferred metal component is lanthanum. The inorganic oxide support is subjected to steam treatment at temperatures from 38 to 149°C (100 to 300°F) higher than the temperature at which the process is to be operated. Steam treatment reduces the surface area of the support by about 20 percent relative to unsteamed support, and requires lesser amounts of lanthanum sorbent in the sorbent composite, without loss of sorption capacity. After the impregnation of a lanthanum compound (e.g., $La(OH)_3$) on the support, the solid is first dried and then calcined at the process operating temperatures. Promoters such as sodium and potassium can also be incorporated into the support (about 1.3 atoms of promoter per atom of sorption active metal) to increase the sorbent capacity.

A schematic diagram of the Exxon Process is shown in Figure 24. First, absorption is carried out in reactor A and regeneration in reactor B. The feed gas is introduced into the fixed-bed absorber at temperatures between 149° and 927°C (300 and 1700°F) and pressures between 10^5 and 7.8×10^5 Pa (0 and 100 psig). The space velocity is maintained between 300 and 1000 vol. gas/vol. supported sorbent/hour. The supported sorbent removes hydrogen sulfide and acts as a catalyst for the conversion of carbonyl sulfide to hydrogen sulfide with the following "possible" mechanism, based on the formation and decomposition of thio acids:

$$COS + H_2O = H_2CO_2S$$

$$H_2CO_2S = CO_2 + H_2S$$

If lanthanum oxide is used as the active material, then the desulfurization reaction is:

$$La_2O_3 + 3H_2S = La_2S_3 + 3H_2O$$

Regeneration in reactor B is achieved in two steps. In the first step called desorption, the sulfided sorbent is treated with steam or a gas containing steam at absorption temperatures and pressures. The reverse of the absorption reaction takes place. The amount of steam is about 20-40 moles per mole of sorbed hydrogen sulfide. The second step consists of restoring the activity of the sorbent by contacting it with an oxidizing gas, such as air or oxygen, at temperatures used in the sorption cycle. The space velocity is between 500 and 2500 vol. air/vol. supported sorbent/hour. The off-gas from this second step may contain small amounts of sulfur dioxide and, therefore, be environmentally objectionable for discharging to the atmosphere. Instead, they can be used in the process, possibly in the gasifier (A-13).

When the supported sorbent in reactor A has reached capacity, the regeneration (desorption/activation) operation in reactor B is substantially complete and the reactors are switched; that is, reactor B will go on the absorption cycle while reactor A is on the desorption/activation cycle. Various sorbents and support mater-

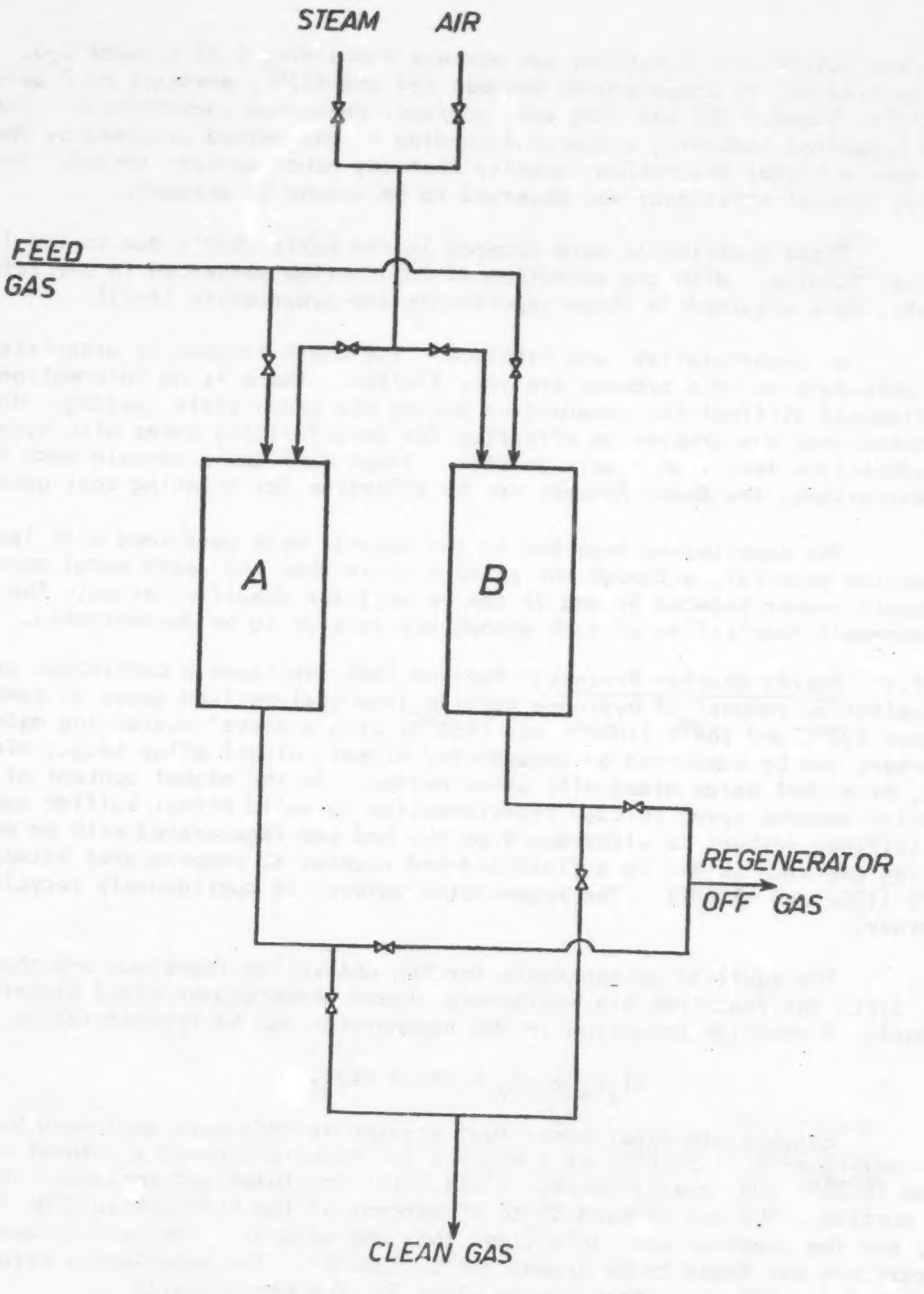

STEAM
AIR
FEED GAS
A
B
REGENERATOR OFF GAS
CLEAN GAS

FIGURE 24. EXXON PROCESS

ials were tested with a bottled gas mixture containing 0.96 percent H_2S. These tests were carried out at temperatures between 538 and 927°C, pressure of 0 psig and space velocities between 700 and 1000 vol. gas/vol. supported sorbent/hour. The lanthanum oxide supported sorbents, prepared according to the method proposed by Wheelock, et al., gave a higher absorption capacity than any other sorbent tested. Hydrogen sulfide removal efficiency was observed to be around 98 percent.

These experiments were dropped in the early 1970's due to the lack of internal funding. With the exception of information presented in the referenced patents, data obtained in these experiments are proprietary (A-13).

- Uncertainties and Problems: The Exxon Process is proprietary, and available data on this process are very limited. There is no information on the experimental difficulties encountered during the bench-scale testing. However, it is indicated that the process is effective for desulfurizing gases with hydrogen sulfide concentrations less than 3 mole percent. Since coal gases contain much lower H_2S concentrations, the Exxon Process may be effective for cleaning coal gases.

The experiments reported in the patents were performed with lanthanum as the active material, although the patents claim that any earth metal component with an atomic number between 57 and 71 can be used for desulfurization. The technical and economic feasibility of such absorbents remains to be demonstrated.

3.1.5.2 Foster Wheeler Process: Steiner (49) describes a continuous process for the selective removal of hydrogen sulfide from coal-derived gases at temperatures between 538°C and 788°C (1000°F and 1450°F) with a nickel-containing material. The absorbent can be supported or unsupported nickel, nickel alloy (e.g., nickel-aluminum), or nickel oxide mixed with other oxides. As the nickel content of the sorbent material becomes spent through transformation to solid nickel sulfide compounds, the sulfided sorbent is withdrawn from the bed and regenerated with an oxygen-containing gas such as air in a fluidized-bed reactor at temperatures between 538 and 732°C (1000 and 1350°F). The regenerated sorbent is continuously recycled into the absorber.

The equilibrium constants for the absorption reactions are shown in Figure 25. Since the reactions are exothermic, lower temperatures yield higher sulfur removal. A reaction occurring in the regenerator can be represented as:

$$Ni_xS_y + yO_2 = xNi + ySO_2.$$

Bench-scale experiments that started in 1974 were performed by passing 0.10 normal m^3/h (3.5 SCFH) of a bottled gas mixture through a sorbent bed in a 22 mm (0.86") I.D. quartz reactor (A-14,15). The inlet gas contained 4500 ppm hydrogen sulfide. The bed removed 85 to 95 percent of the hydrogen sulfide from the inlet gas, and the reaction was rapid (less than one second). The optimum desulfurization temperature was found to be around 704°C (1300°F). The experiments were later discontinued in 1976, and there are no plans for further research.

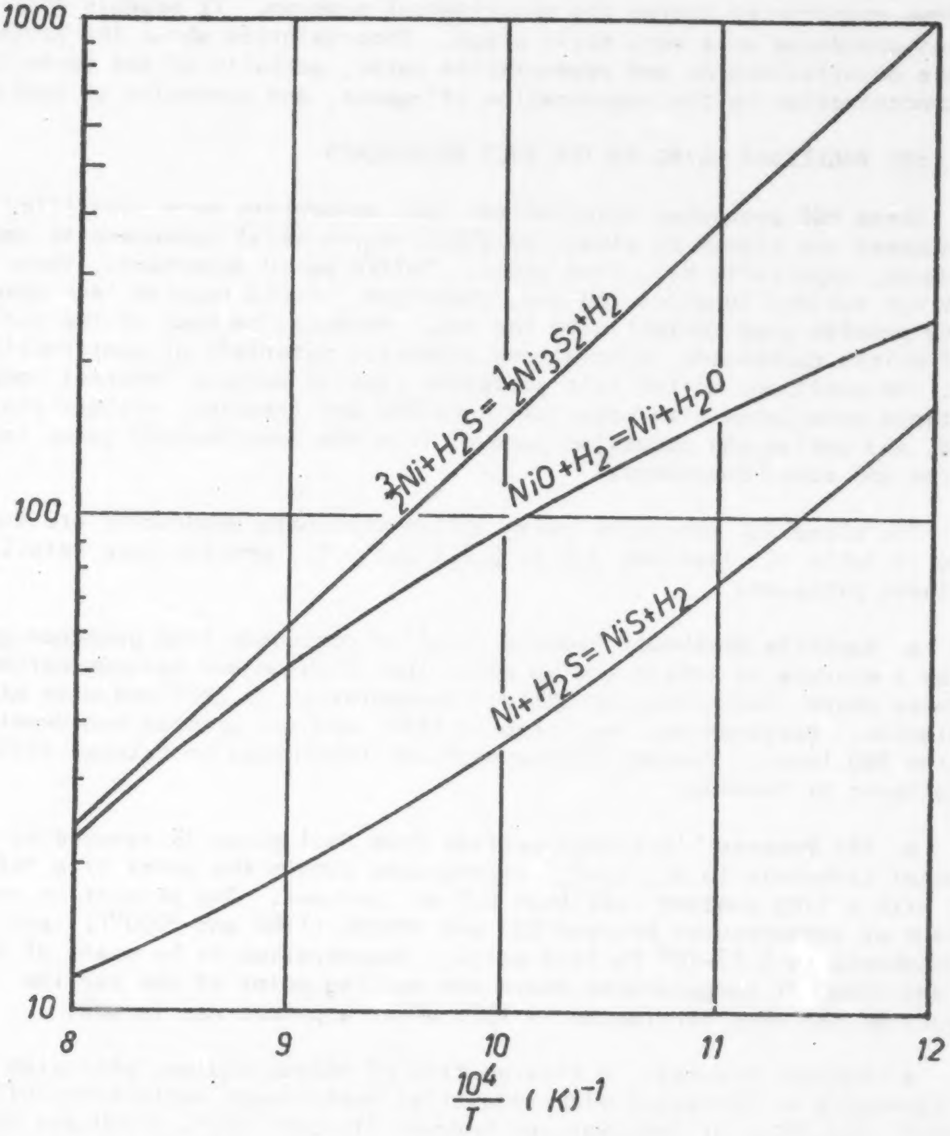


FIGURE 25. EQUILIBRIUM CONSTANTS FOR Ni-CONTAINING SORBENTS

- Uncertainties and Problems: No information was available concerning the problems encountered during the experimental program. It appears that the process was abandoned at a very early stage. Uncertainties about the process would include the desulfurization and regeneration rates, activity of the sorbent, sulfur dioxide concentration in the regeneration off-gases, and corrosion of equipment.

3.2 HGC PROCESSES USING MOLTEN SALT ABSORBENTS

Three HGC processes using molten salt absorbents were identified. All three processes use either an alkali or alkali-earth metal carbonate to remove sulfur compounds, especially H_2S, from gases. Unlike solid absorbents, these molten salts are not subject to attrition and, therefore, should require less make-up. Also, they provide good contact with the gas. However, because of the corrosive nature of molten carbonates, special and expensive materials of construction would be required. In addition, molten salt processes involve certain inherent complications, such as those associated with materials handling and transfer, process start up and shut down, and sodium and potassium removal from the desulfurized gases to protect gas turbine and other components.

The three HGC processes using molten carbonate absorbents are summarized below and in Table 10. Sections 3.2.1, 3.2.2 and 3.2.3 provide more detailed information on these processes.

- Battelle Northwest Process: Sulfur compounds from producer gas are removed by a mixture of molten sodium potassium, lithium and calcium carbonates at temperatures above 600°C in a scrubber. Regeneration is achieved with steam and carbon dioxide. Research was initiated in 1972, and the process was developed through the PDU level. Process development was terminated in October 1978 due to the curtailment of funding.

- HRI Process: Hydrogen sulfide from fuel gases is removed by a molten alkali-metal carbonate (e.g., K_2CO_3) impregnated within the pores of a refractory material with a SiO_2 content less than 2.0 wt. percent. The absorption reaction takes place at temperatures between 927 and 1093°C (1700 and 2000°F), and pressures from atmospheric to 4.18×10^6 Pa (600 psig). Regeneration is by means of carbon dioxide and steam at temperatures above the melting point of the sulfide. Bench-scale tests at HRI were terminated in 1976 after a patent was issued.

- Pullman Process: A flowing film of molten sodium, potassium and/or lithium carbonate is contacted with industrial waste gases containing sulfur compounds (H_2S, SO_2, SO_3) at temperatures between 816 and 1093°C (1500 and 2000°F) and pressures between 1×10^5 and 5×10^5 Pa (1 and 5 atm). Regeneration consists of solidification, dissolution in water, filtration and dehydration of the sulfided melt.

3.2.1 Battelle Northwest Process

The Battelle research program, which started in November 1972 under a contract with the Office of Coal Research, focused on cleaning hot fuel gas by molten salt scrubbing. The project was unfunded between December 1974 and October 1975.

TABLE 15 - HGC PROCESSES USING MOLTEN SALT ABSORBENTS

HGC PROCESSES	STATUS	ABSORBENT	ABSORPTION TEMP. (°C)	PRESSURE (Pa)	GAS FLOW RATE normal m^3/h	METHOD OF REGENERATION	REGENERATION TEMPERATURE (°C)	COMMENTS
Battelle Northwest	Terminated	Li, Na, K Ca Carbonates	600-910	1×10^5	127	H_2O-CO_2	500-600	PDU Operated
HRI	Terminated	Supported K_2CO_3/ Na_2CO_3	907-1093	1.2×10^6 4×10^6	0.01	H_2O-CO_2	907-1093	
Pullman	Terminated	Li, Na, K carbonates	816-1093	1×10^5 5×10^5		Metal Bicarbonate - CO_2		

The U.S. Department of Energy then supported this research program until October 1978, at which time the process development work was terminated. There are no plans for further research.

The development of the Battelle Process has undergone three phases. First, bench-scale tests were carried out to study various selected H_2S absorbents. Second, PDU tests were conducted to demonstrate the H_2S absorption characteristics under batch mode of operation. Finally, a PDU was constructed for continuous operation to demonstrate both the absorption and regeneration steps of the process.

The Battelle Northwest Process is patented by Moore (50).

Bench-Scale Experiments (51): Bench-scale experiments were performed in an alumina-lined Inconel 600 bubbler contactor having a capacity of about 1 liter of molten salt and accepting flows up to 10 ℓ/min. The synthetic produces gas in the tests was slightly above 10^5 Pa (1 atm) pressure and contained 20 percent (by volume) H_2, 20 percent CO, 15 percent CO_2, 45 percent N_2, and 0.5 percent H_2S. Early experiments conducted with a binary eutectic of $CaCl_2$:NaCl as a solvent for $CaCO_3$ (or CaO) at temperatures up to 850°C, where CaO solubility is 7-8 mole percent, exhibited good absorption and regeneration performance with respect to H_2S. However, the vapor pressure of NaCl is too high to permit its use in turbine applications.

Tests with molten Na_2CO_3 at around 850°C showed almost complete extraction of H_2S from moist synthetic fuel gas, although corrosion of the Inconel 600 scrubber was observed. Efficient regeneration could not be achieved at temperatures above the melting point of Na_2CO_3 (854°C) since chemical equilibria do not favor reversal of the extraction reaction at such temperatures.

A ternary eutectic mixture of equal weights of Li_2CO_3, Na_2CO_3, and K_2CO_3, with a melting point of 393°C (741°F) also showed excellent extraction of H_2S (above 95 percent). Figure 26 shows the dependency of the equilibrium constant, calculated from experimental results, on temperature for the ternary mixture. The data for the absorption of H_2S with Na_2CO_3 are also included in Figure 12 for comparison. Regeneration of the spent ternary mixture was achieved with a mixture of 75 percent H_2O and 25 percent CO_2, at a salt temperature of 854°C. In the first two hours, 84.5 percent of the total H_2S evolved at an average steam utilization of 31.4 percent. Again, severe corrosion was observed.

Separate corrosion tests were conducted with various alloys in the ternary eutectic mixture discussed above, sparged with H_2S. About 1.5 percent of the carbonate was converted to sulfide. The corrosion test results of two 50-hour exposures are presented below:

Alloy	Corrosion Rate, mils/month (1 mil=25.4µm) Period 1	Period 2
347SS	0.5	1.6
Haynes 25	1.5	1.2
50 Cr-50 Ni	0.2	1.9
HAPO-20	0.2	1.4
Hastelloy F	1.1	0.6

Another set of experiments were performed with 15 percent (by weight) $CaCO_3$, mixed with equal parts (by weight) of potassium, lithium and sodium carbonates. Approximately 50 percent of the $CaCO_3$ was converted to CaS by sparging with H_2S. High density Al_2O_3 ceramics, type 406 SS, and some alonized steels were found to be corrosion resistant. With alonized 304 SS, the penetration rate was found to be 2.54 μm/month (0.1 mil/month).

Further bench-scale absorption tests were performed with a molten salt mixture containing 27.3 percent (by weight) Li_2CO_3, 26.5 percent Na_2CO_3, 27.5 percent K_2CO_3, and 18.8 percent $CaCO_3$, at temperatures between 600 and 910°C and atmospheric pressure. The experimental data showed that the addition of $CaCO_3$ substantially improved the removal of H_2S. Regeneration of the spent salt was almost complete, although steam utilization was poor. In two hours, 71.5 percent regeneration was achieved with 10 percent steam utilization. Further tests were performed with a reduced concentration of Li_2CO_3 (about 13 percent by weight), since Li_2CO_3 is the most expensive of the salt ingredients. The result was an absorption of H_2S in the range of 90 to 99^+ percent, with a maximum of 63 percent consumption of the available $CaCO_3$.

It was concluded from these bench-scale tests that the mixed alkali carbonates, containing about 15-20 mole percent $CaCO_3$, are excellent sorbents for H_2S. The equilibrium constant calculated from experimental results for the quaternary mixed carbonates is given in Figure 26 as a function of temperature. In the salt mixture, $CaCO_3$ is the most reactive ingredient, with the absorption reaction occurring between $CaCO_3$ and H_2S until most of the $CaCO_3$ is consumed.

The general reaction between H_2S and the molten carbonate can be expressed as follows:

$$MCO_3\ (\ell) + H_2S_{(g)} = MS\ (\ell) + CO_2(g) + H_2O(g),$$

where M represents the metal. Regeneration can be accomplished by reversing this reaction. If both the liquid and gas phases are ideal, then the equilibrium constant for the above reaction can be expressed as follows:

$$K = \left(\frac{X_{MS}}{X_{MCO_3}}\right)\left(\frac{Y_{CO_2}\ \ Y_{H_2O}}{Y_{H_2S}}\right)(P)$$

where X_i is the mole fraction of compound i in the liquid gas,

Y_i is the mole fraction of compound i in the gas phase, and

P is the total pressure.

Batch-Mode PDU Experiments: The design of the PDU for batch-mode operation (50) is based upon a once-through flow of the gas and cyclic use of the quaternary salt mixture. The experiment was designed to purify 1.42-2.12 normal m^3/h (50-75 SCFM) of producer gas, generated from Battelle Northwest's fixed-bed gasifier. The

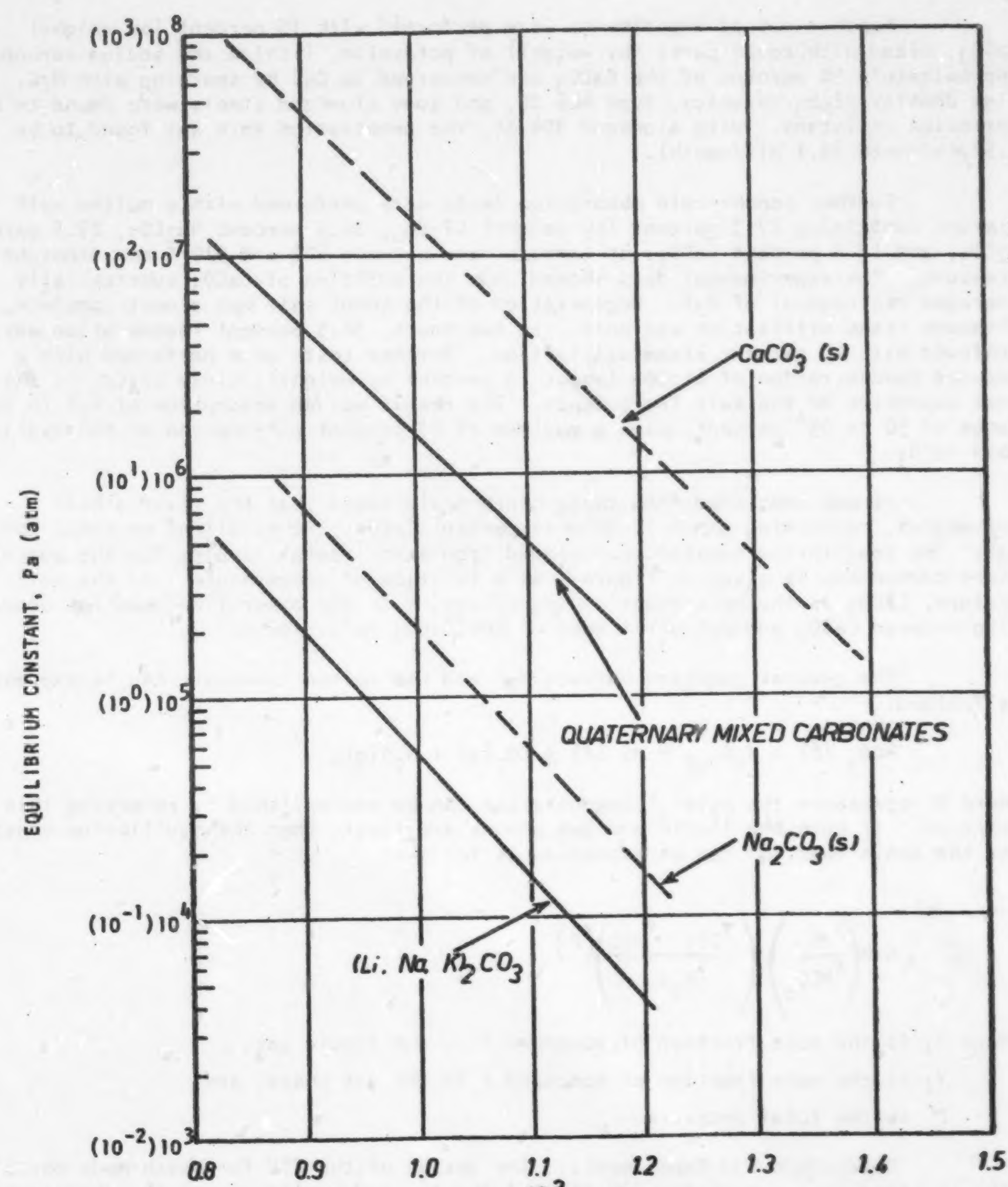


FIGURE 26. TEMPERATURE DEPENDENCE OF EQUILIBRIUM CONSTANTS FOR REACTIONS BETWEEN H_2S AND MOLTEN CARBONATES

temperature of the exit gas from the gasifier was in the range of 204-427°C (400 - 800°F), and the pressure was 10^5 Pa (1 atm). Since the producer gas was not quite as hot as desired, an electrically powered heater was provided to preheat the gas. The H_2S concentration of the gas was adjusted to 0.65 percent (by volume). The inventory of the salt was 75.7-94.6 dm^3 (20-25 gallons) enough to allow 4-6 hours operation. Alonized type 304 SS was selected as the material of construction. A block diagram of the PDU is shown in Figure 27.

The gas heater is adjusted to heat the gasifier exit gas from 427°C up to 900°C. The molten salt mixture, from Pot Furnace 1, flows to the vertically oriented venturi scrubber, where it is atomized and entrained in the gas. The venturi scrubber is designed to yield above 99 percent collection efficiency of particles $4 \mu m$ or larger. The salt and gas mixture is carried to the deentrainment and demister section located above Pot Furnace 1, under a gravity induced flow. Clean gas flows to the burner where it is combusted and then vented. For regeneration, the gas flow is stopped and all salt is collected in Pot Furnace 2, where the salt is cooled to 550-580°C, and reacted with carbon dioxide and steam. The H_2S rich off-gas from Pot Furnace 2 is then contacted with a sodium carbonate solution in a packed bed scrubber. A sodium hydrosulfide solution is formed according to the following reaction:

$$Na_2CO_3(\ell) + 2H_2S(g) = NaHS(\ell) + CO_2(g) + H_2O(g),$$

and is then disposed. The regenerated salt is lifted back into Pot Furnace 1 with nitrogen.

The salt composition was 13.0 percent (by weight) Li_2CO_3, 36.0 percent Na_2CO_3, 37.3 percent K_2CO_3, and 13.7 percent $CaCO_3$ in these batch PDU tests. At 749°C (1380°F), the H_2S recovery was between 94 and 97 percent. This recovery rate agrees with data developed during the bench-scale testing. The $CaCO_3$ utilization ranged between 16.7 and 29.5 percent. In a set of runs at higher temperatures (around 820°C), $CaCO_3$ dissociated, forming CaO as a precipitate, after its solubility was exceeded. In these tests, 99 percent H_2S removal was achieved. However, the presence of COS in the product gas limited overall sulfur removal. No corrosion of the alonized steel equipment and piping was observed. The particle removal efficiency, as well as the particle size distribution, was obtained through sampling. The product gas contained approximately 12 ppm salt, which is about an order of magnitude higher than the acceptable level for turbine fuel.

Continuous-Mode PDU Tests: The continuous mode PDU (52) was designed to demonstrate that the salt can be continuously regenerated, simultaneous with the extraction of sulfur compounds and particles from producer gas. The equipment design is shown in Figure 28. As in the batch design, the venturi scrubber is used to lift the gas-salt dispersion to the deentrainer; therefore, no mechanical pump is required. The inlet gas produced in the gasifier flows at 85-212 normal m^3/h (50-75 SCFM) and its H_2S concentration is adjusted to 1.3 percent. The design of the venturi scrubber is such that the gas velocity at the throat is 76 m/s (250 ft/s). The salt contains a mixture of lithium, sodium and potassium carbonates. Calcium carbonate was not incorporated in this mixture because of its tendency to decompose and precipitate at elevated temperatures.

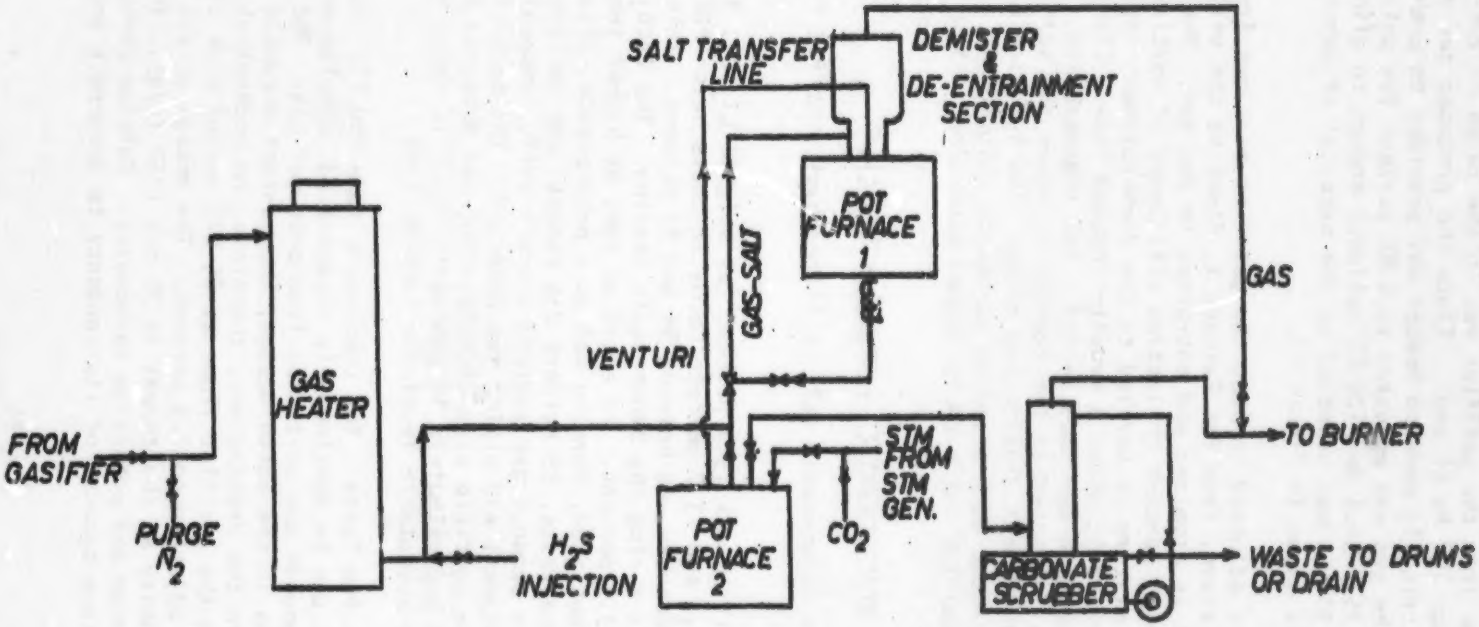
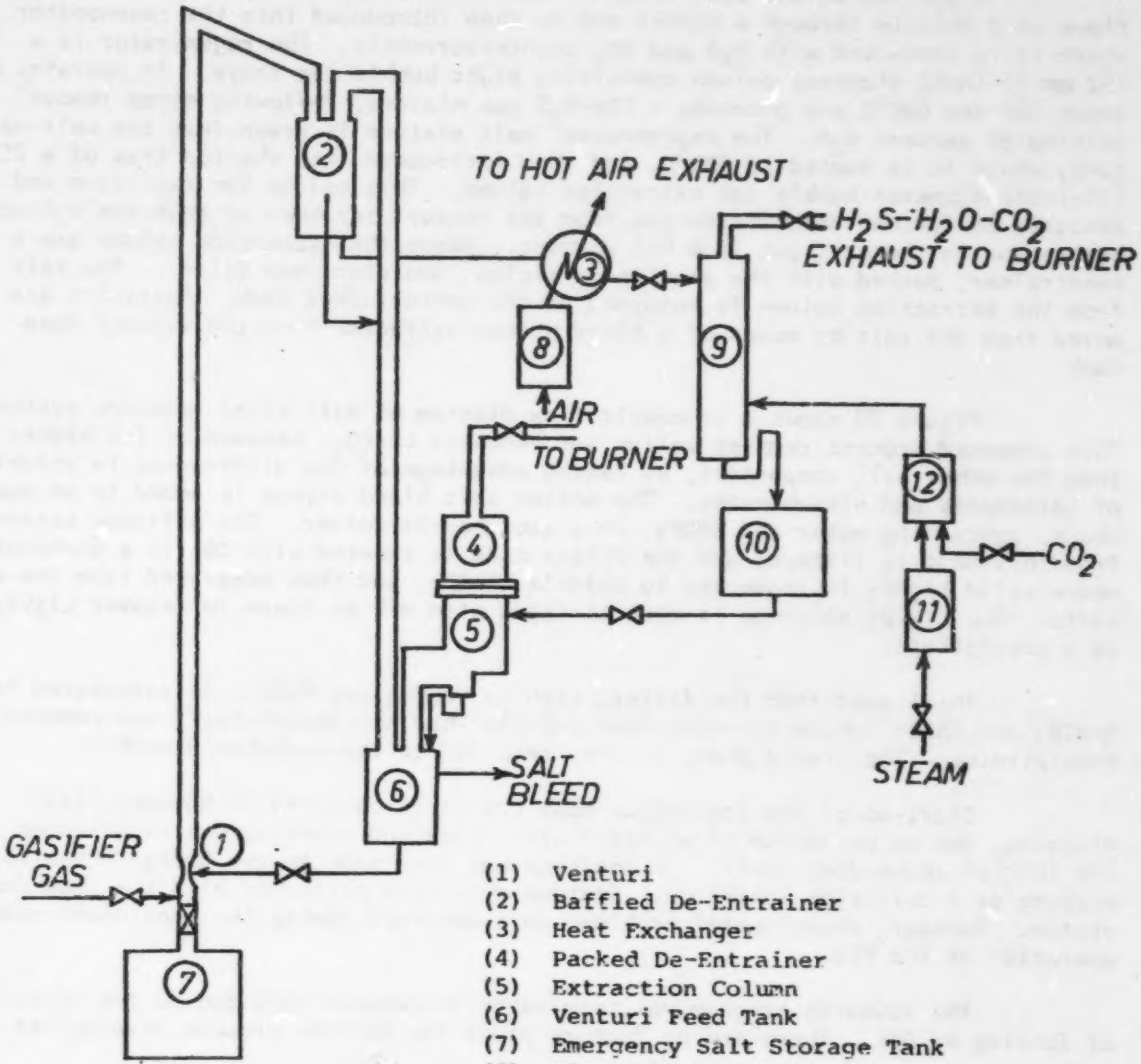

FROM GASIFIER
PURGE N_2
GAS HEATER
H_2S INJECTION
VENTURI
SALT TRANSFER LINE
GAS-SALT
POT FURNACE 1
POT FURNACE 2
DEMISTER & DE-ENTRAINMENT SECTION
STM FROM STM GEN.
CO_2
CARBONATE SCRUBBER
GAS
TO BURNER
WASTE TO DRUMS OR DRAIN

FIGURE 27. BATCH-MODE TEST APPARATUS


TO HOT AIR EXHAUST
$H_2S-H_2O-CO_2$
EXHAUST TO BURNER
AIR
TO BURNER
SALT
BLEED
GASIFIER
GAS
CO_2
STEAM
1
2
3
4
5
6
7
8
9
10
11
12

(1)	Venturi
(2)	Baffled De-Entrainer
(3)	Heat Exchanger
(4)	Packed De-Entrainer
(5)	Extraction Column
(6)	Venturi Feed Tank
(7)	Emergency Salt Storage Tank
(8)	Air Preheater
(9)	Regenerator
(10)	Salt Make-Up Tank and Reheater
(11)	Steam Preheater
(12)	Steam and CO_2 Preheater

FIGURE 28. CONTINUOUS-MODE TEST APPARATUS

A portion of the salt removed from the deentrainer by inertial impaction flows at 3 dm^3/min through a cooler and is then introduced into the regenerator, where it is contacted with H_2O and CO_2 countercurrently. The regenerator is a 152 mm (6-inch) diameter column containing eight bubble cap trays. It operates between 500 and 600°C and produces a CO_2-H_2S gas mixture, following steam removal, containing 30 percent H_2S. The regenerated salt mixture is drawn into the salt make-up tank, where it is heated to 700°C, and then introduced into the top tray of a 254 mm (10-inch) diameter bubble cap extraction column. This column has two trays and is designed to further desulfurize gas from the venturi scrubber so that the H_2S concentration in the exit gas is 0.045 percent. Above the extraction column are a deentrainer, packed with the alumina particles, demister, and filter. The salt from the extraction column is returned to the venturi feed tank. Particles are removed from the salt by means of a bleed stream extracted from the venturi feed tank.

Figure 29 shows a schematic flow diagram of salt bleed recovery system (53). This proposed process removes solids and recovers Li_2CO_3, because of its higher cost than the other salt components, by taking advantage of the differences in solubility of carbonates and bicarbonates. The molten salt bleed stream is added to an aqueous phase, containing water and $KHCO_3$, in a quencher-dissolver. The effluent stream from this unit is filtered and the filter cake is treated with CO_2 in a carbonator, where solid Li_2CO_3 is converted to soluble $LiHCO_3$, and thus separated from the solid waste. The $LiHCO_3$ solution is then stripped with air or steam to recover Li_2CO_3 as a precipitate.

The liquid from the filter, rich in Na_2CO_3 and K_2CO_3, is carbonated to $NaHCO_3$ and $KHCO_3$ (which are much less soluble than the carbonates), and removed as precipitates. The liquid phase is then recycled to the quencher-dissolver.

Start-up of the continuous-mode PDU (A-16)occurred in November 1977. Plugging, due to corrosion of alonized steel pipe and vessels, was experienced during the initial shake-down tests. A decision was then made to use $CaCO_3$ in the salt mixture as a corrosion inhibitor. Sixteen runs were performed with the four-component system. However, experimental problems were observed during the continuous-mode of operation of the PDU.

The research program was terminated in October 1978 due to the curtailment of funding by DOE. There are no furture plans for further process development.

- Uncertainties and Problems: The use of a pump was avoided by incorporating a venturi scrubber which atomizes the molten liquid by means of the product gas and raises the liquid-gas mixture to a higher level. This process is the first in which the use of a molten liquid was attempted in a venturi scrubber. In the continuous PDU shake-down tests, erosion of the throat of the venturi scrubber was observed. The eroded materials, along with the corrosion materials from the alonized steel equipment and piping, deposited and plugged the valve and the venturi feed line. To prevent this problem, a filter trap was designed, but has not yet been tested. Battelle decided to conduct further PDU testing with a quaternary mixture of carbonate, introducing $CaCO_3$ into the lithium, sodium, and potassium carbonate

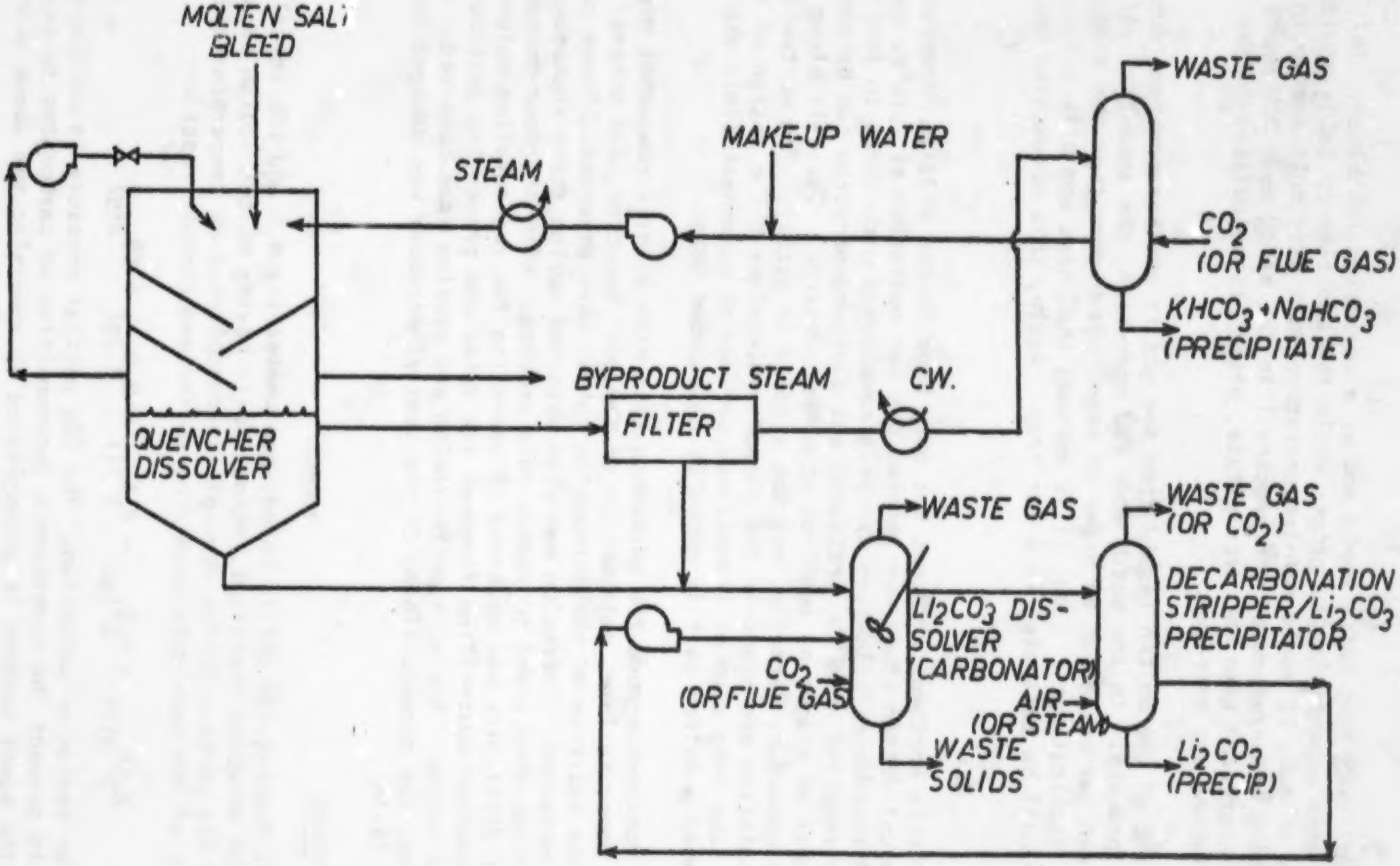

MOLTEN SALT BLEED
STEAM
MAKE-UP WATER
WASTE GAS
CO_2 (OR FLUE GAS)
$KHCO_3 + NaHCO_3$ (PRECIPITATE)
BYPRODUCT STEAM
C.W.
FILTER
QUENCHER DISSOLVER
WASTE GAS
Li_2CO_3 DIS-SOLVER (CARBONATOR)
CO_2 (OR FLUE GAS
WASTE SOLIDS
WASTE GAS (OR CO_2)
DECARBONATION STRIPPER/Li_2CO_3 PRECIPITATOR
AIR (OR STEAM
Li_2CO_3 (PRECIP.)

FIGURE 29. SCHEMATIC FLOW DIAGRAM OF SALT BLEED RECOVERY

mixture. It was believed that $CaCO_3$ would act as a corrosion inhibitor. This, however, has not yet been experimentally proven while the addition of $CaCO_3$ would improve the recovery of H_2S, it would make regeneration more difficult and would limit the maximum operating temperature of the process. In the batch mode PDU operation at 820°C, $CaCO_3$ dissociated into CaO precipitate, after its solubility in the quaternary salt mixture was exceeded.

Separation of the molten liquid from the gas is another problem, due to the nature of the process. In the batch mode PDU operation, the amount of salt remaining in the clean gas was about an order of magnitude higher than the acceptable level for turbine applications. Also, it is assumed that tars and oils originating from the gasifier will be collected in a tar trap. Again, this assumption has yet to be tested.

The Battelle Northwest Process has only been tested at 10^5Pa pressure. However, a conceptual design study was carried out for operation at $2x10^6$Pa pressure. It was calculated that desulfurization can be accomplished with three to four times as many stages as required at 10^5Pa pressure, and that regeneration can be achieved with half the number of stages as required at 10^5Pa pressure. The salt bleed section of the process, proposed by Battelle, was not studied in detail. The molten liquid and the aqueous solution are mixed in the quencher-dissolver. The design of this equipment should take into account the serious problem of superheat limit explosions which can occur when a molten salt is added to an aqueous phase.

In the continuous-mode PDU shakedown test with a three component mixture, problems such as power failure, malfunction of the coal conveyor, and others associated with the start-up of the extraction column were observed. These problems were eventually corrected. Corrosion was also observed during these shakedown tests. Calcium carbonate was then added to remedy this problem. With the four-component system, the major difficulty was observed in operating the regeneration column. Other problems involved controlling flows at low rates and preventing particulates from plugging the valves. Again, some corrosion and erosion were observed. Finally, during the testing, the ceramic lining of the venturi scrubber was damaged due to thermal stresses (A-16).

3.2.2 HRI Process

The HRI Process (54,55) is based upon contacting H_2S and COS containing fuel gases with an abrasion resistant, porous solid having molten sodium or potassium carbonate within its pores. Sulfur removal is accomplished at temperatures above the melting point of the carbonate according to the endothermic reaction:

$$M_2CO_{3(l)} + H_2S_{(g)} = M_2S_{(l)} + H_2O_{(g)} + CO_{2(g)}$$

where M stands for sodium or potassium. The CO_2 partial pressure is maintained at such a level as to prevent the endothermic decomposition of carbonates to oxides. Regeneration of the spent sorbent is accomplished by reversing the above absorption reaction.

The HRI Process, shown in Figure 30, is described by Wolk, et al (55). Producer gases generated by the reaction of steam and oxygen with coal or oil are introduced into a fluidized-bed absorber for desulfurization. The absorber contains a strong, abrasion resistant, porous particulate material, such as aluminum oxide, with potassium carbonate dispersed within its pores. The operating conditions for the absorber are 927-1093°C (1700-2000°F) and about 1.5×10^6-4.2×10^6 Pa (200-600 psig) pressure. The sulfur compounds in the hot fuel gas are reacted with the molten potassium carbonate within the pores of the particulate absorbent to form potassium sulfide. The substantially sulfur-free fuel gas is then passed through a gas-solid separation unit, in which particulates are removed. The resulting fuel gas can then be combusted with compressed air and expanded in a turbine for power generation.

As the absorption capacity of potassium carbonate is substantially depleted, the absorbent is regenerated by withdrawing a portion of it from the fluidized-bed absorber and passing it to the regenerator. There, the absorbent is regenerated in a fluidized bed with pressurized steam and carbon dioxide. The regeneration temperature is sufficiently high so as to maintain the potassium sulfide in a molten condition, such as 927-1093°C. The regenerated absorbent is then returned to the fluidized-bed absorber. The gas stream from the regenerator is further treated to recover sulfur. The process can employ moving-bed or dual-fixed beds instead of fluidized-bed reactors.

Impregnation of the liquid carbonates into the pores of a strong solid offers several advantages. First, it reduces the corrosive effects of the melt. Secondly, absorption and regeneration take place without involving the crystalline structure of the solid support; therefore, attrition of the support material is not promoted. Thirdly, this system allows for good gas sorbent contact, and provides high heat transfer rates to sustain the rapid endothermic desulfurization reaction.

Laboratory experiments were initially performed with unsupported molten potassium carbonate. These experiments revealed complete removal of H_2S from a gas containing 5 percent H_2S and 95 percent H_2 at 927-1093°C, 10^5 Pa pressure, and with a space velocity of 460 vol. gas/vol. melt/h. Complete regeneration of the melt was not achieved with equimolar steam and carbon dioxide because of the presence of oxygen entering the system with the steam, thereby converting the sulfide to sulfate.

An experiment was also made in a 22 mm (7/8") I.D. alumina reactor at 927°C. The reactor bed was packed with 6.4 mm (1/4") diameter alumina and silica supported sorbents containing 12.6 percent K_2CO_3. About 11.3 dm^3/h (0.4 ft^3/h) of gas containing 5 percent hydrogen sulfide in hydrogen was passed through the reactor at a space velocity of 460 vol. gas/vol. bed/h. There was no evidence of physical degradation of solids when the absorption period was over. However, in an experiment in which the supported sorbent contained 16.3 percent K_2CO_3, physical degradation of the support material was observed. Formation of the water soluble metasilicate was suspected from the reaction of silica in the support with potassium carbonate:

$$SiO_{2(s)} + K_2CO_3(\ell) = K_2O.SiO_{2(s)} + CO_{2(g)}.$$

Another experiment was performed in the same fixed bed reactor at 954°C (1750°F) by contacting 18 wt. percent K_2CO_3 in the same support material with an inlet gas mixture containing 1.2 percent hydrogen sulfide in hydrogen. More than 95 percent of the H_2S was removed. Regeneration was achieved with equimolar amounts of steam

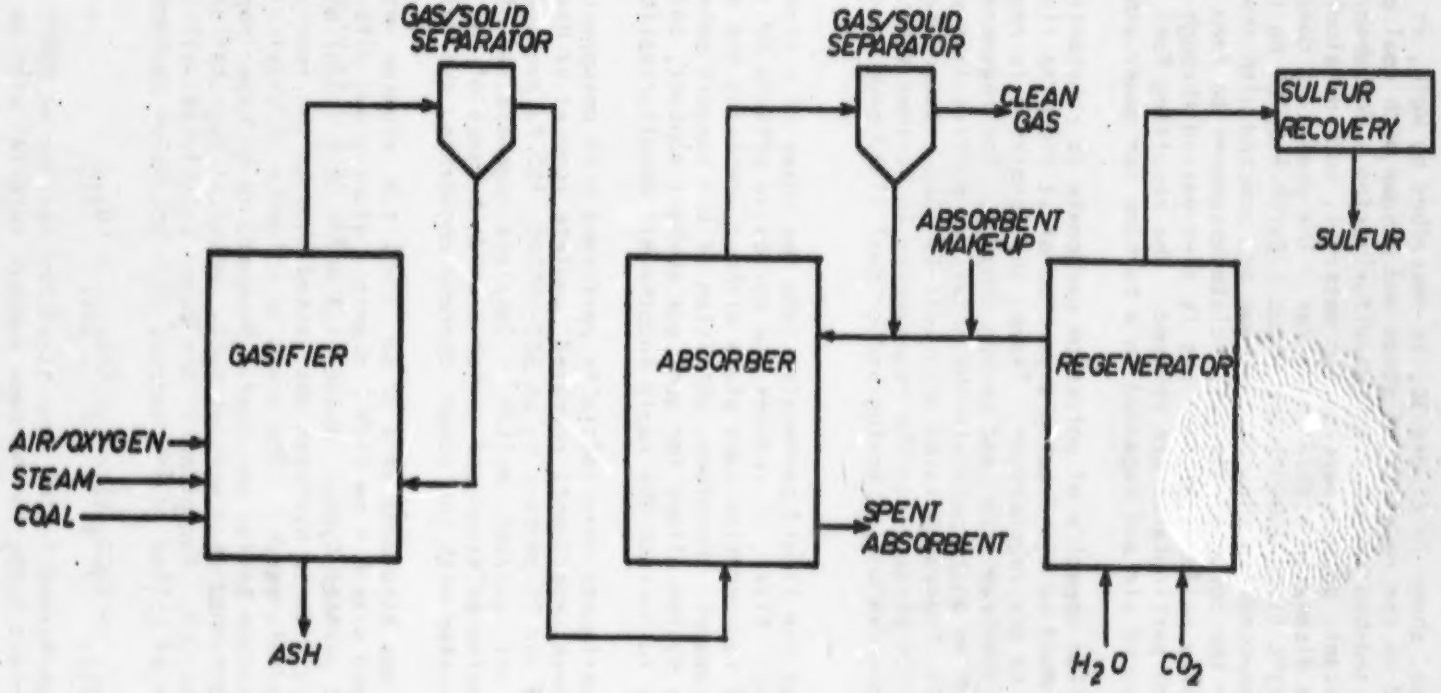

GAS/SOLID SEPARATOR
GAS/SOLID SEPARATOR
CLEAN GAS
SULFUR RECOVERY
SULFUR
ABSORBENT MAKE-UP
GASIFIER
ABSORBER
REGENERATOR
AIR/OXYGEN
STEAM
COAL
SPENT ABSORBENT
ASH
H_2O
CO_2

FIGURE 30. HRI PROCESS

and carbon dioxide. However, the formation of sulfate could not be prevented and, during the two following absorption cycles, removal efficiencies dropped to 63 percent and 39 percent. Upon examination of the inside of the reactor after the experiment, migration of the melt from the silica, as well as fusion of particles to each other (formation of metasilicate), were observed.

Experimental work was terminated when the patent was issued. There are presently no plans to do further work on this process due to a lack of funding and the uncertain potential for commercialization of hot gas cleanup processes in general (A-17).

- Uncertainties and Problems: Although both references state that removal of H_2S can be achieved with either potassium or sodium carbonate, or a mixture of the two, experimental work was carried out only with potassium carbonate. Thus, sodium carbonate and mixtures of the two carbonates were not tested.

Complete regeneration was never achieved. The reason was apparently due to the formation of potassium sulfate by the oxygen dissolved in the water employed to produce the steam used for regneration. This sulfate was then converted to sulfide by hydrogen:

$$K_2SO_4(\ell) + 4H_{2(g)} = K_2S_{(\ell)} + 4H_2O_{(g)}.$$

Formation of metasilicate due to the reaction between silica and potassium carbonate, was a problem when the support material contained 13.4 percent silica:

$$SiO_2 + K_2CO_3 = K_2O.SiO_2 + CO_2 \quad .$$

This was prevented by using a support material containing high purity alumina with a very low silica content (0.4 wt percent).

The problem of migration of melt from the pores of the alumina was never resolved, but the inventors believe that it can be prevented if both desulfurization and regeneration are carried out in a fluidized-bed reactor.

3.2.3 Pullman Process

The Pullman Process, invented be Lefrançois, et al. (66), was developed to remove sulfur compounds (H_2S, SO_2, SO_3), nitrogen compounds, and fly-ash from industrial waste gases by means of molten sodium, potassium and/or lithium carbonates at temperatures between 816 and 1093°C (1500 and 2000°F) and pressure between $1x10^5$ and $5x10^5$ Pa (1 and 5 atm). The gas and liquid are contacted in chambers, where a moving film of liquid is deposited on alumina trays, and the gas is directed by means of baffles. Pressure drop is maintained less than $1x10^4$ Pa (1.5 psi) to eliminate the entrainment of liquid droplets into the gas stream. The absorption scheme is shown in Figure 31.

The preferred regeneration procedure is described in U.S. Pat. 3,567,377. According to this procedure, the sulfided melt is diluted with an aqueous solution of the metal bicarbonate. If necessary, it is filtered to remove solids from the

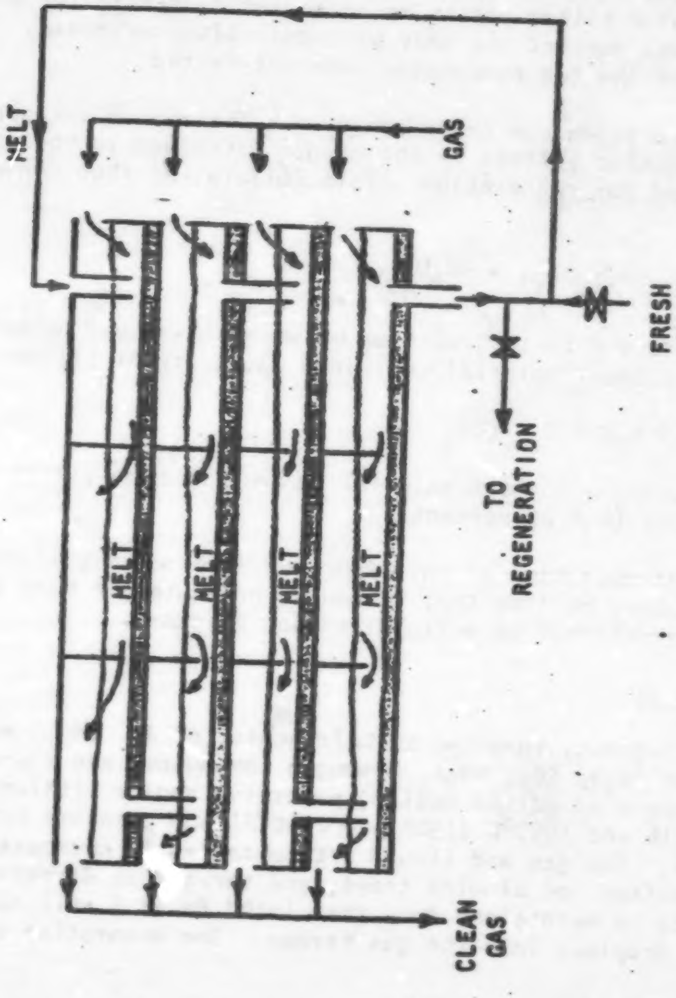

MELT
GAS
FRESH MELT
TO REGENERATION
MELT
MELT
MELT
MELT
CLEAN GAS

FIGURE 31. PULLMAN PROCESS

resulting solution. Then, this solution is passed into a two stage carbonation zone. In the first stage, any carbonate in the solution is converted to bicarbonate precipitate by contact with a carbon dioxide gas. This treatment results in a more viscous and less alkaline solution. The solution is then passed to the second stage, where it is contacted with carbon dioxide gas for removal of sulfur values as hydrogen sulfide. Finally, a portion of the bicarbonate is converted to carbonate, which is heated and recycled for absorption.

An experiment was performed at about 948°C (1740°F) by bubbling a gas mixture of 1 percent hydrogen sulfide in nitrogen through molten sodium carbonate at a velocity of 15 cm/s (0.5 ft/s) and a pressure drop of 10^4 Pa. The exit nitrogen from the demister zone was initially found to contain less than 5 ppm of carbonate and hydrogen sulfide.

- Uncertainties and Problems: The information obtained on the Pullman Process is very limited. A corrosion problem was observed during the testing. After 30 minutes of operation, the stainless steel demister filter required replacement due to heavy corrosion. Experimental data concerning the regeneration of the sulfided melt is not given in the patent from which this information was obtained.

3.3 HGC PROCESSES USING MOLTEN METAL ABSORBENTS

Only the IGT-Meissner Process has been identified in this group. This process, under development by the Institute of Gas Technology, is ongoing at the bench-scale level. In this process, molten lead is sprayed into a reducing gas containing hydrogen sulfide at temperatures between 327 and 1200°C (621 and 2192°F). The lead - lead sulfide slurry formed from the absorption reaction is electrolyzed to regenerate lead and obtain sulfur. In general, this process has similar advantages and disadvantages of processes using molten salt absorbents. A detailed description of the IGT Process is presented in Section 3.3.1.

3.3.1 IGT-Meissner Process

The IGT-Meissner Process employs molten lead to remove hydrogen sulfide from hot reducing gases. This proprietary process is being developed and funded by the Institute of Gas Technology (IGT) in conjunction with its U-Gas Process (57). Information from IGT (A-18) reveals that the present lab-scale research is basically along the same lines as the process described in the patent, issued to Meissner (58).

The desulfurization reaction between the molten lead and the hydrogen sulfide in reducing gases can be represented as follows:

$$Pb + H_2S = PbS + H_2 \qquad (1)$$

Figure 32 shows the variation of the equilibrium constant for this reaction with respect to temperature. Whether or not the incoming gas is reducing depends upon the mole ratios of CO_2/CO and H_2O/H_2. These ratios are important in minimizing the formation of lead oxide according to the following reactions:

$$PbO + CO = Pb + CO_2 \qquad (2)$$

$$PbO + H_2 = Pb + H_2O \qquad (3)$$

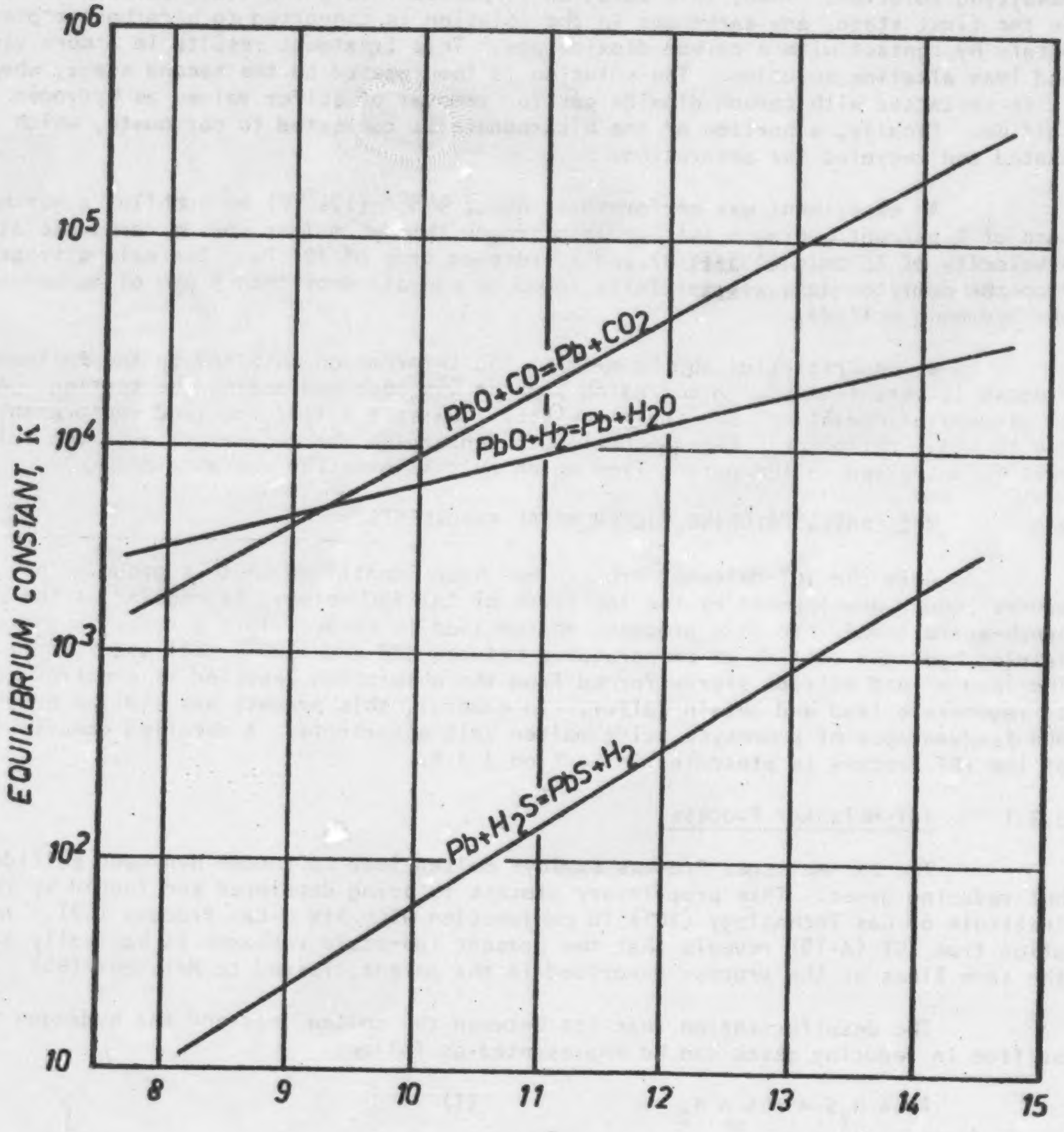


FIGURE 32. EQUILIBRIUM CONSTANTS FOR DESULFURIZATION WITH LEAD ABSORBENTS

The two ratios are related through the water gas shift reaction:

$$H_2O + CO = H_2 + CO_2 \qquad (4)$$

Equilibrium information on reactions (2) and (3) is also included in Figure 32.

A schmatic flow diagram of the IGT-Meissner Process is shown in Figure 33.

Desulfurization can be achieved by various contact methods at temperatures between 327°C (621°F, melting point of lead) and 1200°C (2192°F). The preferred method, described in the patent and shown in Figure 33 consists of spraying a shower of droplets through the flowing gases passing through the reaction chamber. A rotating disk or paddle wheel, partially immersed in the metal pool in the bottom of the chamber, can be used to spray the droplets through the gas. Providing that the H_2O/H_2 and CO_2/CO ratios are of proper magnitude, undesirable oxides do not form and molten lead retains its ability to react with sulfur. The lead sulfide which is formed dissolves in the liquid until the saturation point is reached, at which time additional sulfide precipitates. The amount of sulfide formed is important with respect to the pumpability of the slurry. Figure 34 shows a temperature/composition diagram for the lead-lead sulfide system.

Regeneration can be achieved by various methods. One method involves roasting the lead sulfide to oxide, and then reacting the oxidized lead compound with more lead sulfide to form metallic lead and sulfur dioxide. Lead oxide may also be reduced to lead when reacted with carbon, hydrogen or carbon monoxide. The regeneration method discussed in detail in the patent and shown in Figure 33 utilizes electrolysis. The cell uses molten lead as the cathode and a carbon rod as the anode. The carbon rod is dipped in an electrolyte layer of lead chloride or an alkali metal salt (such as potassium chloride or sodium sulfide), in which lead sulfide is soluble. Sulfur forms at the anode, either in liquid or gaseous form, depending upon the operating conditions. Molten lead in the melt is returned for absorption in amounts sufficient not only to react with all the sulfur compounds, but also provide a pumpable slurry with lead sulfide present.

An experiment was performed at 426°C (800°F) by passing fuel gas containing 0.3 percent H_2S and 0.1 percent COS through a spray of molten lead. The amount of lead recycled to the desulfurization chamber was 0.82 kg/m^3 (51 lb/1000 ft^3) of gas treated. Sulfur removal efficiency was above 50 percent in this experiment. Regeneration was achieved by electrolysis in a chloride solution, with sulfur being released in gaseous form.

- Uncertainties and Problems: Since the IGT-Meissner Process is proprietary, the available information on this process is very limited. The major anticipated problems include corrosion of vessels, transfer lines, pumps and valves. Difficulties in equipment shut-downs due to the solidication of the molten metal and plugging of the transfer lines, pump and valves might also be expected.

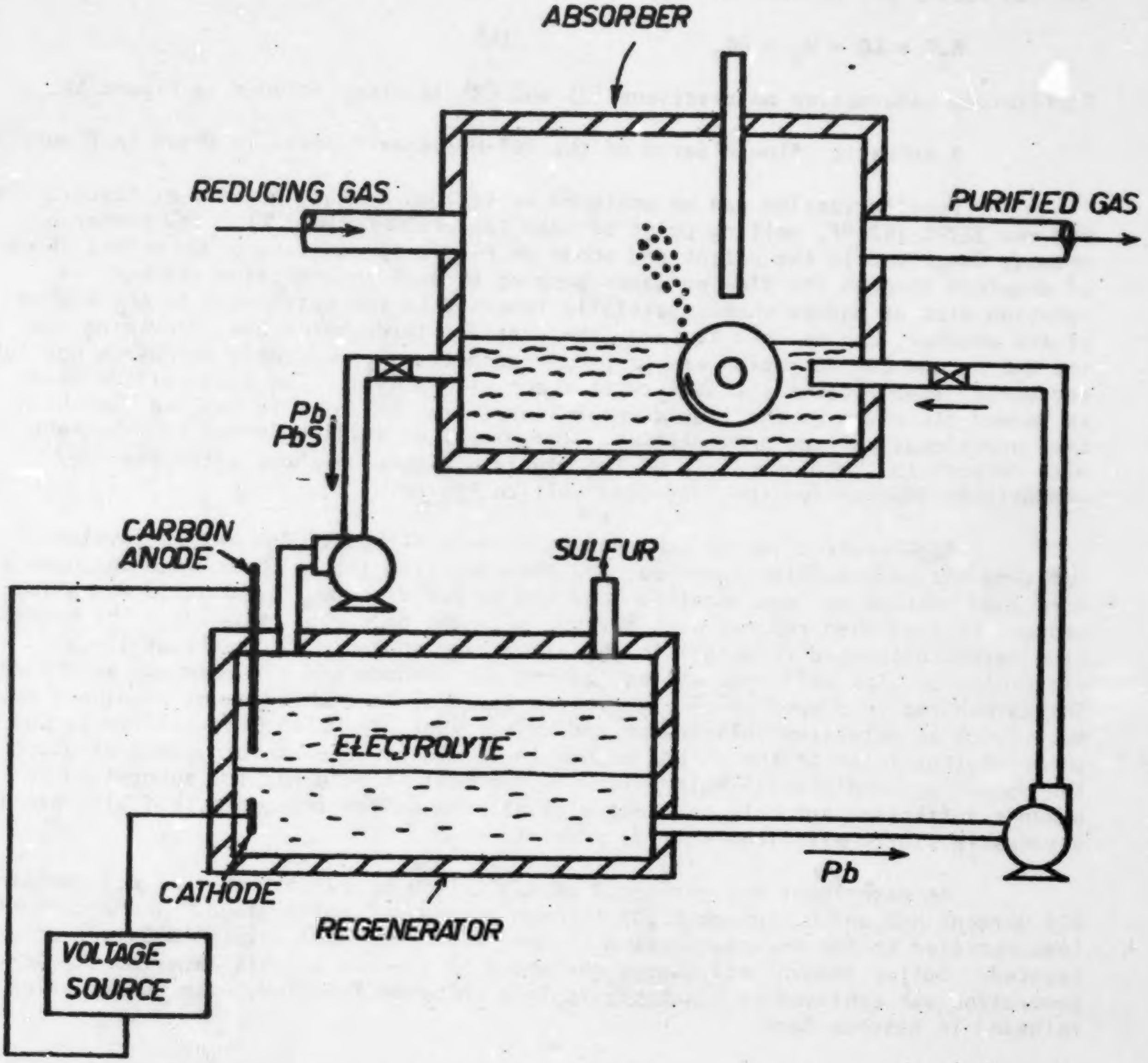

ABSORBER
REDUCING GAS
PURIFIED GAS
Pb
PbS
CARBON ANODE
SULFUR
ELECTROLYTE
Pb
CATHODE
REGENERATOR
VOLTAGE SOURCE

FIGURE 33. IGT-MEISSNER PROCESS

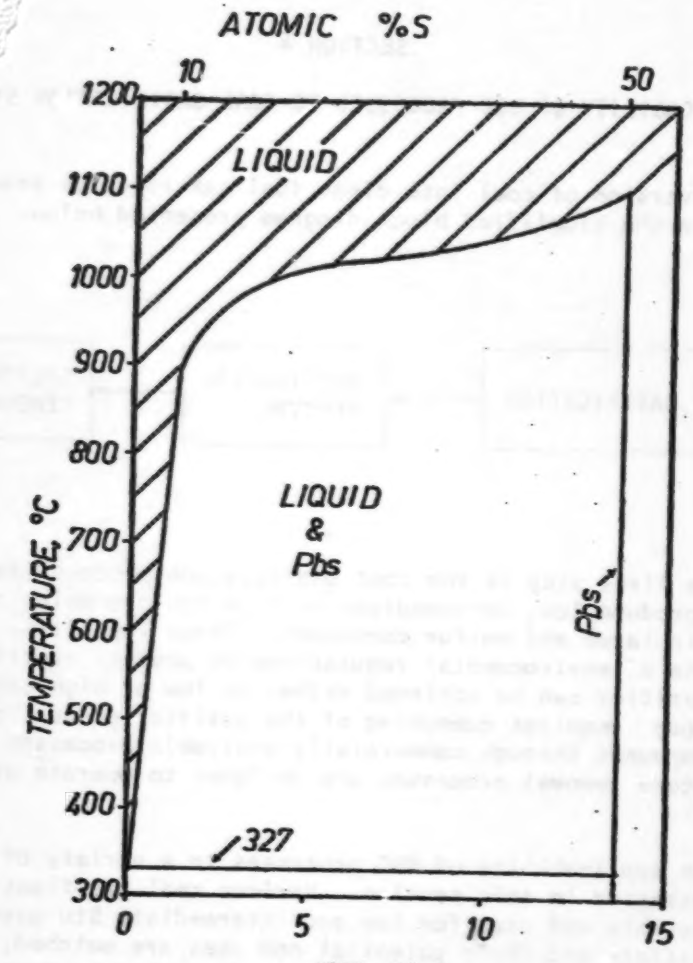
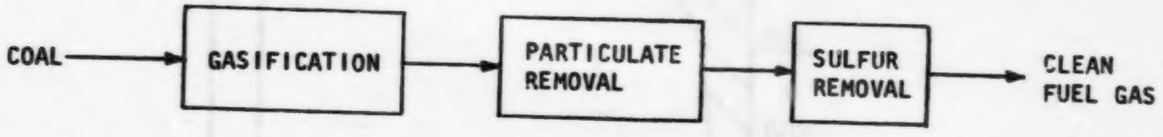


FIGURE 34. TEMPERATURE/COMPOSITION DIAGRAM FOR LEAD-LEAD SULFIDE SYSTEM

SECTION 4

APPLICABILITY OF HGC PROCESSES TO COAL GASIFICATION SYSTEMS

Conversion of coal into clean fuel gas requires several process steps as illustrated in the simplified block diagram presented below.



The first step is the coal gasification process itself. The gasification of coal can produce low, intermediate or high Btu gas which contains impurities such as particulates and sulfur compounds. These impurities can be objectionable either because of environmental regulations or process restrictions. The removal of these impurities can be achieved either at low or high temperature. Low temperature cleanup requires quenching of the gasifier product gas, as well as removal of sulfur compounds through commercially available processes. On the other hand, high temperature removal processes are designed to operate at temperatures above 427°C (800°F).

The applicability of HGC processes to a variety of coal gasification systems is assessed in this section. Various coal gasification processes are reviewed, possible end uses for low and intermediate Btu gases are evaluated, the types of gasifiers and their potential end uses are matched, and finally the applicability of the hot gas cleanup processes described in Section 3.0 to the gasifier-end use pairs is evaluated. The use of HGC processes to clean high Btu gases is not considered in this study, since it would not be economically possible to transport these gases at high temperatures over long distances.

4.1 GASIFIERS

Many gasifiers have been developed, and some have been commercially used to produce low and intermediate Btu gases from coal. Table 11 shows a list of promising low and intermediate Btu gasifiers and their characteristics. Low and intermediate Btu gasifiers can be classified as:

TABLE 11

PROMISING LOW AND INTERMEDIATE BTU GASIFIERS

TYPE OF GASIFIER	GASIFICATION MEDIUM		PRESSURE	
	(Low Btu) Air/H_2O	(Int. Btu) O_2/H_2O	Low	High
Fixed Bed				
Lurgi	x			x
Wellman-Galusha	x	x	x	
Chapman (Wilputte)	x	x	x	
Woodall-Duckham/Gas Integrale	x	x	x	
Foster Wheeler/Stoic	x	x	x	
MERC	x			x
BGC/Lurgi Slagging		x		x
GFERC Slagging		x		x
Riley Morgan	x	x	x	
Fluidized Bed				
Winkler	x	x	x	
Entrained Bed				
Koppers-Totzek		x	x	
Coalex	x		x	
Bi-Gas	x	x		x
Texaco	x	x		x
Foster Wheeler	x	x		x

- fixed bed gasifiers,
- fluidized bed gasifiers, and
- entrained bed gasifiers

Below is a brief description of each generic gasifier type, including the characteristics of the pollutants present in the raw product gas.

4.1.1 Fixed Bed Gasifiers

In the fixed or moving bed gasifiers, coal is introduced at the top of the gasifier and contacted countercurrently with a mixture of air or oxygen and steam. This gas mixture is admitted to the gasifier beneath the grate supporting the coal bed. The bed is maintained at a fixed level and the flow of solids can be described as essentially plug flow. The gas solid contact results in various zones in the bed. At the top zone coal is heated and devolatilized. Below that is the gasification zone where carbon in the coal reacts with steam and carbon dioxide to produce carbon monoxide and hydrogen. The third and bottom zone is the combustion zone, in which a portion of coal is burned to provide the heat necessary for the endothermic reactions in the gasification and devolatilization zones. Fixed bed gasifiers have the advantage of providing high carbon conversion with high energy efficiencies, but are generally limited to non-coking coals at specified size ranges.

Several fixed bed gasifiers including the Wellman-Galusha, Chapman (Wilputte), Woodall Duckham/Gas Integrale and Lurgi have been commercially used. Among these, the Lurgi gasifier is the only one employed at high pressures.

The distribution of sulfur compounds in the exit streams from a Lurgi gasifier tested on American coal was determined as a percentage of the sulfur present in the feed coal. The sulfur balance is shown below (59):

	Percent of inlet sulfur
H_2S in gas stream.	92.0
Organic sulfur compounds in gas stream	1.5
Sulfides in condensate	2.5
Tars/oils.	2.5
Gasifier bottom ash.	1.5

The gasifier bottom ash showed the widest variation, containing up to 6% of the feed sulfur in coal in some cases. About 1 to 2% of the feed sulfur was in the form of organic sulfur compounds.

Fixed bed gasifiers also produce tars and oils which condense at low temperatures. The amount of these hydrocarbons and organic compounds in the raw gas depends upon the type of coal feed and gasifier operating conditions. Lower gasifier temperatures and pressures enhance the formation of heavier hydrocarbons. About 40 to 75 grams of condensable hydrocarbons per kilogram (80-150 lb/ton) of moisture and ash free (MAF) coal, or 16-34 g/normal m^3 (7-15 grains/SCF) of raw product gases, is reported from tests with American coals in a Lurgi gasifier (60).

Fixed bed gasifiers generate lower particulate loadings in the raw product gas than entrained and fluidized bed gasifiers. Particulate loadings from fixed bed gasifiers range from about 0.9 to 5.7 g/normal m^3 (0.4 to 2.5 grains/SCF). The size distribution data in the Lurgi runs on American coals indicate that 40-80% of particulates is under 100 μm (60). Other data obtained from the MERC fixed bed gasifier (61) tests show that 50-70% of the particles collected in cyclones are under 150 μm in size. These particles contain about 75 to 80%, and sometimes up to 90% of devolatilized coal char, the remainder being coal ash. The Lurgi data show that coal ash in the raw gas represents 0.5% of the ash in the feed coal (60).

The fate of nitrogen in the feed coal was also determined from tests on American coals in a Lurgi gasifier (60). About 60% of the nitrogen in the feed coal appeared in the raw gas as NH_3, 35% as N_2 and the rest in tars and oils. It was also found that the raw gas contained 5-50 ppm by volume HCN and that the bottom ash from the gasifier did not retain any nitrogen.

4.1.2 Fluidized Bed Gasifiers

In a fluidized bed gasifier, the gas flows upward through the coal particles at a high enough rate to maintain the bed in suspension. The vigorous solids movement in the gasifier enables intimate solid-gas mixing, which provides a uniform bed temperature. Gasification reactions are primarily a combination of combustion and water-gas reactions at temperatures of 816 to 1093°C (1500 to 2000°F). Substantial quantities of char are produced when gasification is not achieved to completion. The advantages of fluidized bed gasifiers are their high gasification rates and excellent heat transfer characteristics which prevent the formation of clinkers, and ability to handle a large variety of coals with respect to quality and size.

Winkler is the only fluidized bed gasifier which has been commerically used. However, much more information is available from fluid bed gasifiers under development than from the Winkler gasifier.

There are limited data available concerning the distribution of sulfur compounds in various streams from fluidized bed gasifiers. The percentage of sulfur gasified is reported to be greater than the percentage of carbon gasified (62). Data from the Winkler gasifier show that more than 96-97% of the feed sulfur is present in the raw gas (63) (64). The sulfur compounds in the raw gas are primarily in the form of H_2S, with some organic sulfur compounds (carbonyl sulfide, methyl mercaptan and ethyl mercaptan) also present (65).

Due to its high operating temperature (about 1700°F), the Winkler gasifier does not produce any tars and heavy hydrocarbons, and the presence of phenols and light hydrocarbons in the raw gas has not been reported (63) (66). Similar results were obtained from tests with the bench-scale Hygas fluidized bed gasifier (65). Data indicate that about 38 grams of light oil (benzene, toluene) per kilogram of dry coal feed may be present in the raw gas. However, in tests with the bench-scale

Synthane fluidized bed gasifier (steam/oxygen gasification), it was found that coal type and coal injection geometry significantly affect the amount of tars produced. For example, 8-38 g tar/kg MAF coal was obtained with North Dakota lignite, whereas 45-80 g tar/kg MAF coal was obtained with Illinois #6 and Pittsburgh coals (67).

Fluidized bed gasifiers produce high particle loadings in the gas streams due to the high gas velocities of 1.5-3.1 m/s. Data from tests with Winkler gasifier show particle loadings of about 114g/normal m^3(50 grains/SCF). These particles contain about 70% ash and 30% carbon (63). Similar results are reported from tests with the Hygas gasifier (68). However, particle loadings of 4.6-11.4 g/normal m^3 (2-5 grains/SCF) are reported from tests with Synthane gasifier (69), which does not gasify coal to completion but produces a char by-product.

No information is available on nitrogen compounds from the Winkler gasifier. Conversion of up to 70% of the feed nitrogen from coal to NH_3 is reported for Hygas (70) and Synthane (67) processes.

4.1.3 Entrained Bed Gasifiers

Entrained bed gasifiers use pulverized coal, and are characterized by low inventory of fuel in the reaction zone. The temperature and, therefore, the gasification rate decrease from inlet to outlet of the gasifier. For this reason it is not economically feasible to gasify more than 85 to 90% of the carbon in a single pass. However, higher carbon conversions can be achieved by recycling the solid residue.

The major advantage of entrained bed gasifiers is their ability to handle any type of coal with no concern about the particle sizes and caking characteristics. Also, the overall energy production rate per reactor volume is higher than for other types of gasifiers. However, the need for recovery of heat and chars from these gases to achieve high overall thermal efficiency are drawbacks for the entrained bed gasifiers.

Among the various entrained bed gasifiers, the Koppers-Totzek gasifier is the only one that has been used commercially. Gasification has been carried out for the production of hydrogen in ammonia synthesis. There are no commercial installations of the Koppers-Totzek gasifier in the United States.

Information on impurities from entrained bed gasifiers is very limited. For the Koppers-Totzek gasifier (71), sulfur in the feed coal appears mainly in the raw gas stream as H_2S with some COS and SO_2. Condensable hydrocarbons are not present since they are cracked to gaseous constituents at high gasification temperatures above 1093°C (2000°F). The particulate loading in the raw gas from the Koppers-Totzek gasifier is reported to be 27.5-55.0 g/normal m^3 (12-24 grains/SCF). It is also reported that the raw gas contains both NH_3 and HCN, although thermodynamics favors the decomposition of ammonia into nitrogen and hydrogen at high temperatures.

4.2 POTENTIAL END USES FOR LOW AND INTERMEDIATE BTU GASES

In 1976, the electric utility and industrial sectors together contributed 55 percent of the energy consumed in the United States. Natural gas and petroleum supplied 80 percent of the energy input to industry and 30 percent to the electric utilities(72) The use of coal-derived gases to replace natural gas and petroleum in these areas could have important economic benefits in the United States, in addition to reducing the nation's dependency on foreign, unreliable sources of energy. The following sections examine how these two energy sources are used in the industrial and electric utility sectors, and whether they can be replaced by low and intermediate Btu gases.

4.2.1 Industrial Applications

Natural gas and petroleum provide 80 percent of the energy input to industry, primarily for use as:

- fuel for direct process heat,
- fuel for small and industrial size boilers to raise steam,
- fuel for gas turbines, and
- reducing gas for the reduction of iron ore and regeneration gas for some catalysts and sorbent materials; synthesis gas.

4.2.1.1 Direct Process Heat: Low and medium Btu coal gases appear to be applicable as fuel for direct process heat in the petroleum refining, chemical and allied products, primary metals, glass, cement, lime, ceramics, and possibly other industries.

In the petroleum refining industry, low and intermediate Btu gases have potential application in some areas where natural gas or oil is presently fired. They can be especially used in tube-type furnace heat exchangers which are designed to heat the feedstocks for various operations such as distillation, cracking and reforming.

In the chemical and allied products industry, the bulk of process heat from fossil fuels is used in firing furnaces. These furnaces have tube-type heat exchangers fired externally, with chemical feed inside the tube in much the same manner as watertube boilers, and would be adaptable to either low or intermediate Btu gas firing.

In the iron and steel industry coal-derived gas was used in open hearth furnaces about fifty years ago to provide the heat required for the production of steel from iron. Today, natural gas and oil are used for this purpose. Shifting to coal gases again probably would not cause any major difficulty. Another area where coal gases can easily be substituted for natural gas is in preheating the air combusted in blast furnaces for the production of pig iron from iron ore. This represents about 10% of the total energy used for preheating the air (73). Also, about half of the energy required to heat the steel ingots prior to being forged, drawn or extruded into desired shapes, is currently supplied with natural gas, which can be replaced with coal gases with no major difficulty.

About 80 percent of the energy input to ferrous foundries is used in melting ferrous charges in furnaces. These furnaces include cupolas (coke, fired), open hearths (gas and oil fired), air furnaces (pulverized coal fired), reverberatory furnaces (gas and oil fired) and electric furnaces. Open-hearth and reverberatory furnaces would be the two potential applications for low and intermediate Btu coal gases, which represents about 15% of the total energy usage in ferrous foundries.

Among the primary nonferrous metal industries, the aluminum industry consumes the most energy, primarily in the form of electricity and natural gas to calcine alumina trihydrate to anhydrous alumina in rotary kilns at about 1200°C. Other major industries with extensive use of oil and natural gas include the primary copper, zinc and lead industries. Conversion from natural gas and/or oil to coal gases would not present great difficulties.

In the glass industry, about 75-80% of the process energy is consumed for glass melting and is provided by either natural gas or electricity. Conversion of the melters to low energy gas from air-blown gasifiers would be difficult, and the trend is towards electric heating.

In the cement industry, most of the energy is consumed in rotary kilns for the production of clinker, and is provided by pulverized coal, oil or natural gas. Conversion from natural gas or oil to low or intermediate Btu coal gases would require readjustment of the combustion process in the kiln, to maintain a desired flame pattern.

In the lime industry, low or intermediate Btu coal gases could be used in rotary-hearth kilns to calcine limestone or dolomite. Retrofitting of these kilns would require readjustment of the combustion process, which would be less critical than in the cement industry, since combustion takes place outside the kilns.

The ceramics industry produces a variety of products, including brick, clay refractories, ceramic tile and pottery. Low or intermediate Btu gases could be used for firing kilns and various baking and drying operations. Conversion from the present fuel sources (natural gas and oil) to low and intermediate Btu gases from coal should not present any serious difficulty.

4.2.1.2 Industrial Boilers: Industrial boilers represent another potential application of low and intermediate Btu gases, since at least half of the energy input to the industrial sector is used for steam generation, either for process use or on-site electricity generation (59). Industrial boilers can be classified into two types: (1) fire-tube boilers, where combustion gases are passed through tubes immersed in water, and steam is raised outside of the tubing; and (2) water-tube boilers, where steam is raised by passing water through the tubes, with combustion taking place outside of the tubing. Fire-tube boilers have sizes of 159-12,530 kg steam/h (350-27,600 lb/h), and can withstand pressures up to

2×10^6 Pa (300 psi). Water-tube boilers have sizes ranging from 4,540 to over 454,000 kg steam/h (10,000 1,000,000 lb/h), and are suited for pressures between several hundred and 1.36×10^7 Pa (2,000 psi).

Conversion of industrial boilers burning natural gas or oil to low or intermediate Btu gases would require development of suitable burners. Also, due to the increase in gas volumes, especially for low Btu gases, pressure drops would be high and may require redesign of the boiler.

4.2.1.3 Gas Turbines: Gas turbines burn fossils fuels in the combustor section of the turbine to generate electricity. Gas turbines used in industry are more rugged and can handle lower grade fuels than those in aircrafts, which operate with fuel gases at pressures between 7.8×10^5 - 1.6×10^6 Pa (100 and 200 psig) and have very stringent fuel gas specifications to prevent corrosion and erosion of turbine materials. Fuel specifications for industrial gas turbine applications are in the nature of engineering estimates. Westinghouse Electric Corporation projects a maximum allowance of 0.041 g/normal m^3 (0.018 gr/SCF) for particle loading (in the inlet fuel gas to the turbine), with no particles greater than 6 μm (74). The maximum allowable amount of sulfur, as estimated by the United Aircraft Corporation (75), is 0.18 mole percent in the fuel gas. In the presence of sulfur compounds, sodium and potassium in the inlet fuel gas form sulfates, which promote corrosion of the turbine blades at temperatures above 1093°C (1200°F). Vanadium oxidizes to vanadium pentoxide, which catalyzes the corrosion of the turbine at temperatures above 816°C (1500°F). Particulates not only cause corrosion and erosion, but also form hard deposits on the turbine blades and reduce the energy conversion efficiency.

Retrofitting of combustor-turbine systems would be easier for intermediate Btu than low Btu gases. For gases having heating values less than 7.45 MJ/m^3 (200 Btu/SCF) new combustors may be necessary, whereas for gases with heating values less than 5.591 MJ/m^3 (150 Btu/SCF), the turbine would be derated due to the lack of sufficient volume to handle the combustion products (73). Furthermore, high pressure fuel gases from coal gasification units would probably require considerable treatment to meet the turbine specifications.

4.2.1.4 Other Industrial Applications: Low and intermediate Btu gases can also be used as a reducing agent in some industries. In the iron and steel industry, iron ore is converted to pig iron in blast furnaces, with coke being employed as the reducing agent. Natural gas is also injected to reduce the coke requirement and represents about half the energy needed in blast furnaces. If low or intermediate Btu gases are to be used instead of natural gas, they should be at a high temperature and contain practically no CO_2 or water vapor to minimize endothermic effects.

Low and intermediate Btu gases can be used in ammonia and methanol synthesis. For ammonia synthesis, a product gas rich in carbon monoxide and hydrogen is required. For methanol synthesis, a nitrogen free gas with a hydrogen to carbon monoxide mole ratio of 2 is desirable.

Low and intermediate Btu gases can be used in the regeneration of catalysts. In the petroleum industry, catalysts employed in catalytic cracking operations are regenerated by burning off the carbon deposited from the oil at a temperature of around 593°C (1100°F) and pressure of 1.7×10^5 Pa (10 psig). For some cases in which additional fuel is required to maintain these conditions, low or intermediate Btu coal gases could have potential as a fuel. Low and intermediate Btu gases can similarly be used to regenerate absorbent materials used in flue gas desulfurization systems.

4.2.2 Electric Utilities

Low and intermediate Btu gases can be used in:

- Base and intermediate load power plants to raise steam in boilers,
- Peak load power plants to generate electricity by means of gas turbines, and
- Combined cycle power plants.

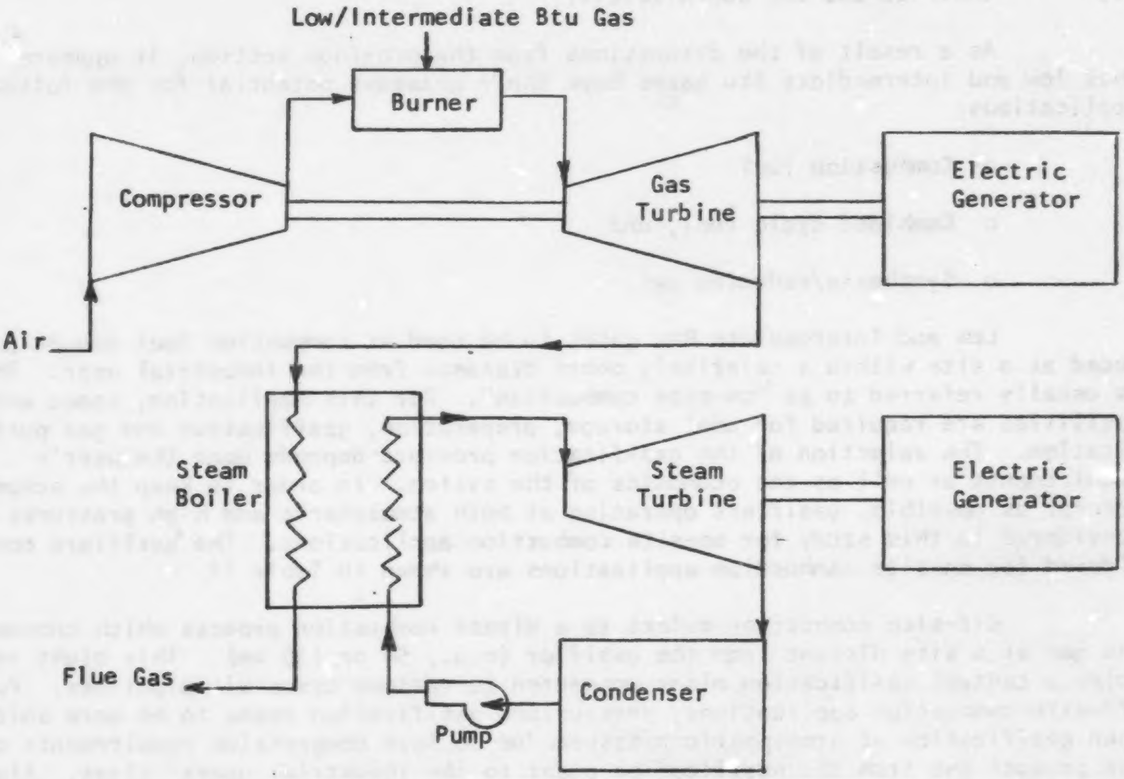
4.2.2.1 Base and Intermediate Load Power Plants: In a base or intermediate load power plant, the fossil fuel (coal, natural gas or oil) is burned with air at atmospheric pressure in a boiler, with the heat of combustion being used to produce high-pressure steam which is expanded in a turbine. The boilers are generally similar to the industrial watertube boilers previously discussed, but are more complicated, much larger and operate at high pressures. Heat transfer in the boilers is provided by two mechanisms: radiation and convection. Radiant heat is transferred directly from the hot flue gases to the banks of tubes which are placed downstream from the combustion zone. The balance between these two heat transfer mechanisms is an important parameter in determining the outlet temperature of steam.

Retrofitting of existing fossil-fueled electric plants to low or intermediate Btu gases appear to have very limited, if any, potential. First, intermediate load plants are operated with frequent shut-downs and start-ups, which would require that the gasifier output be closely controlled to match the power plant demand. For this reason, base load plants which operate continuously are more suited for retrofitting. Second, switching from fossil fuels to low or intermediate Btu gases would create an imbalance in the heat transfer mechanisms in the boiler. This is due to the fact that low and intermediate Btu gases have lower flame luminosity than fossil fuels, and therefore would provide less radiant heat transfer. However, convective heat transfer would be improved. Third, flue gases generated from the combustion of low and intermediate Btu gases are 5 to 12 percent and 30 to 55 percent greater, respectively, than those resulting from fossil fuels. The existing induced and forced draft fans might not be able to handle the increased volumes of flue gases. Since boilers designed for coal are less compact and have wider tube spacings than those designed for natural gas or oil, they would be more attractive for retrofitting to low or intermediate Btu gases than boilers designed for other fuels. However, a study performed by the Tennessee Valley Authority (76) for EPRI shows that firing low Btu gases in retrofitted power plants is not economically competitive with burning coal in conventional power plants and then cleaning up the stack gases. Therefore, the economic incentive appears to favor coal fired conventional power plants, rather than low/intermediate Btu gas-fired power plants.

4.2.2.2 Peak Load Power Plants: Peak load power plants use gas turbines to meet peak electrical demands. They are subject to more frequent start-ups and shutdowns than the intermediate load turbines previously discussed.

Gas turbines used in utilities require gases at pressures greater than 1.5×10^5 Pa (200 psig). The fuel specifications given for industrial gas turbines apply for gas turbines in utilities as well. Retrofitting of these gas turbines to low or intermediate Btu gases would require sophisticated controls not yet available in coal gasification.

4.2.2.3 Combined Cycle Power Plants: Combined cycle power generation appears to have good potential for low and intermediate Btu gas use. In a combined cycle, electricity is produced both by expansion of pressurized gases in a gas turbine and by expansion of steam in a steam turbine. A simplified combined gas-steam turbine system is shown in Figure 35. Low or intermediate Btu gases are burned and then



Low/Intermediate Btu Gas
Burner
Compressor
Gas Turbine
Electric Generator
Air
Steam Boiler
Steam Turbine
Electric Generator
Flue Gas
Condenser
Pump

FIGURE 35. COMBINED CYCLE WITH UNFIRED WASTE HEAT RECOVERY SYSTEM

expanded in the gas turbine, which generates electricity and also drives the air compressor. The flue gases from the turbine are used to deliver heat to the steam boiler, and then released to the atmosphere via the stack. Electricity is also generated from the steam cycle by the expansion of steam in the steam turbine.

Combined cycle power plants (CCPP) are generally more efficient than comparable conventional power plants. A recent study (77) showed that a complete coal gasification - CCPP system would cost up to 15 percent less to build and 20 percent less to operate than conventional coal fired plants. Combined cycle plants have been built and operated in Europe, some of which are the NEWAG plant (55 MW) in Korneuburg, Austria, the EBV-Krafwerk Anna plant and the Hohe Wand plant (75 MV). In addition, there are at least six other combined gas/stream turbine plants in West Germany (78). However, the only CCPP using coal-derived gases is the KDV plant in Lunen, West Germany. This plant gasifies coal at about 2×10^6 Pa (20 atm) in a Lurgi gasifier, and uses a supercharged boiler before expanding the gas in a gas turbine.

4.3 GASIFIER-END USE COMPATIBILITY

As a result of the discussions from the previous section, it appears that low and intermediate Btu gases have their greatest potential for the following applications:

- Combustion fuel
- Combined cycle fuel, and
- Synthesis/reducing gas

Low and intermediate Btu gases to be used as combustion fuel can be produced at a site within a relatively short distance from the industrial user. This is usually referred to as "on-site combustion". For this application, space and facilities are required for coal storage, preparation, gasification and gas purification. The selection of the gasification pressure depends upon the user's requirements as well as the economics of the system. In order to keep the scope as general as possible, gasifiers operating at both atmospheric and high pressures are considered in this study for on-site combustion applications. The gasifiers considered for on-site combustion applications are shown in Table 12.

Off-site combustion refers to a direct combustion process which consumes the gas at a site distant from the gasifier (e.g., 50 or 150 km). This might require a central gasification plant connected to various users via pipelines. For off-site combustion applications, pressurized gasification seems to be more suitable than gasification at atmospheric pressure due to less compression requirements of the product gas from the gasification plant to the industrial users' sites. Also, oxygen blown gasification and transportation systems seem to be more economical than air blown gasification and transportation systems because of the high cost of transporting large volumes of gas. However, since the economics depends upon the transportation distance, both atmospheric and oxygen blown gasifiers are considered in this study for off-site applications. Table 12 shows that Lurgi, MERC, BGC/Lurgi

TABLE 12

GASIFIER - END USE COMPATIBILITY

L: atmospheric pressure
P: high pressure
A: air blown
O: oxygen blown

Gasifiers \ End Uses	On-Site Combustion	Off-Site Combustion	Combined Cycle	Reducing/ Synthesis Gas
Wellman-Galusha	LA LO			
Chapman (Wilputte)	LA LO			
Woodall-Duckham/ Gas Integrale	LA LO			
Lurgi	PA PO	PA PO	PA PO	
Foster Wheeler/Stoic	LA LO			
MERC	PA	PA	PA	
BGC/Lurgi Slagging	PO	PO	PO	
GFERC Slagging	PO	PO	PO	
Riley Morgan	LA LO			
Winkler	LA LO			
Koppers Totzek				LO
Coalex	LA			
Bi-Gas	PA PO	PA PO	PA PO	
Texaco				PA PO
Foster Wheeler	PA PO	PA PO	PA PO	

Slagging, GFERC Slagging, Bi-Gas and Foster Wheeler Gasifiers can be used for off-site applications.

Combined cycle power generation requires expansion of high pressure fuel gas in the gas turbine. For this reason pressurized gasifiers are most applicable. Lurgi, MERC, BGC/Lurgi Slagging, GFERC Slagging, Bi-Gas, Texaco and Foster Wheeler Gasifiers can be used for this application. Both oxygen and air blown gasifiers are considered for combined cycle applications.

For such applications as reducing or synthesis gas, the Koppers-Totzek and Texaco Gasifiers are best suited, since their product gases contain large concentrations of carbon monoxide and hydrogen and small concentrations of hydrocarbons.

4.4 APPLICABILITY OF HGC PROCESSES FOR SELECTED GASIFIER-END USE PAIRS

Seven gasifiers from Table 11 were selected for the purpose of assessing the applicability of the HGC processes over a wide range of gasifier-end use pairs. The selected gasifiers include Lurgi, Wellman-Galusha, MERC, BGC/Slagging, Winkler, Bi-Gas and Foster Wheeler. The first four of these are fixed bed gasifiers, whereas Winkler is fluidized bed and the last two are entrained bed gasifiers. Operation with both air and oxygen were considered for the Lurgi and Foster-Wheeler gasifiers, thereby increasing the number of gasification options to nine. Table 13 shows the operating characteristics of each gasification option, including the effluent wet gas composition.

Particulates present in the raw product gases are assumed to be removed at the gasifier exit conditions. The product gases leaving the particulate collection equipment are then admitted to the HGC equipment for desulfurization. The inlet gas to the HGC equipment can, therefore, be assumed to have the same characteristics as the raw product gases, as presented in Table 13 .

Among the four end uses considered in Table 12 , HGC processes would not seem to couple with off-site combustion applications due to the consideration of transporting the hot gases over long distances via pipelines. For this reason, off-site combustion end uses are not further considered. The clean-up requirements of low or intermediate Btu gases as reducing or synthetic gases depend upon the specific industrial process. For this reason, this end use is not further evaluated. The following discussion is, therefore, pertinent to the applicability of HGC processes for on-site combustion and combined cycle pairs.

The amount of sulfur that must be removed for each gasifier-end use pair was calculated. For on-site combustion applications, the EPA New Source Performance Standards (NSPS) of 0.52 g SO_2/MJ (1.2 lb $SO_2/10^6$ Btu) heat input was employed as the governing limitation on the sulfur content of the product gases. While it is recognized that some states have more restrictive limits than this for new plants and that a less restrictive regulation might apply in many retrofit situations, this NSPS is representative of the regulation that would generally limit the sulfur contents of the product gases. For the combined-cycle applications, both EPA's proposed emission standard and process restrictions were

TABLE 13

CHARACTERISTICS OF SELECTED GASIFICATION OPTIONS

Gasification Medium	Lurgi(79) O_2/H_2O	Lurgi(79) Air/H_2O	Wellman Galusha(80) Air/H_2O	MERC(81) Air/H_2O	BGC/ Slagging(79) O_2/H_2O	Winkler(63) O_2/H_2O	Bi-Gas(92) Air/H_2O	Foster Wheeler(79) O_2/H_2O	Foster Wheeler(79) Air/H_2O
Raw Gas									
CO_2	15.8	9.7	3.0	7.8	1.8	16.3	8.3	12.6	3.4
CO	7.5	11.9	26.0	16.8	54.4	26.4	18.1	34.5	29.2
H_2	20.9	17.1	13.9	13.6	26.9	28.7	13.1	30.1	13.9
CH_4	4.3	2.8	2.5	2.3	7.9	1.3	3.6	6.0	3.4
N_2	0.2	29.6	45.6	41.8	0.4	0.8	45.8	0.4	47.9
H_2S	0.62	0.54	0.70	0.73	1.38	1.10	0.59	1.07	0.65
H_2O	50.3	27.7	8.3	16.7	4.9	25.4	10.2	14.4	2.2
Others	0.4	0.7		0.2	2.3		0.3		0.4
Temperature(°C)	621	549	587	538	427	927	982	927	927
(°F)	1150	1020	1088	1000	800	1700	1800	1700	1700
Pressure(Pa)	$2.0x10^6$	$2.0x10^6$	1x105	$8.5x10^5$	$2.0x10^6$	$1x10^5$	$3.1x10^6$	$2.5x10^6$	$2.5x10^6$
(atm)	20.4	20.4	1+	8.5	20.4	1+	31.0	24.5	24.5
Coal Type	Ill. #6	Ill. #6	Bituminous	Ill. #6	Ill. #6	German Coal	Not Avail.	Ill. #6	Ill. #6
Coal HHV(MJ/kg)	28.5	28.5	27.9*	27.3	28.5	21.7	28.4	28.5	28.5
(Btu/lb)	12,235	12,235	12,000*	11,750	12,235	9,320	12,200	12,235	12,235
wt. %S in Coal	3.9	3.8	>4.0	3.7	3.8	3.3	3.8	3.8	3.8
Gas Prod'n Rate: normal m^3/kg coal**	4.30	4.83	4.95	3.65	1.87	2.19	4.82	2.56	3.99
SCF/lb coal	69.0	77.5	79.3	58.5	29.9	35.1	77.3	41.1	63.9

* Assumed

** Coal; as received

considered. EPA's proposed emission standard for stationary gas turbines is 0.8 weight percent sulfur in the fuel gas (dry basis) burned by turbines (83) (A-19). The gaseous fuel specifications for turbines, based on equipment considerations, is reported to be 0.18 mole percent hydrogen sulfide (84). Table 14 shows the minimum amount of sulfur that must be removed from the product gases to meet the applicable EPA standards or turbine specification. For combustion purposes, at least 79 percent sulfur removal is required for each selected gasifier-end use pair. For combined cycle applications, the turbine specification is more stringent than the proposed EPA standard. Thus the turbine specification was considered as the minimum HGC requirement in assessing the use of HGC processes for combined cycle application. Accordingly, a minimum of 67 to 87 percent of the sulfur in the fuel must be removed, depending upon the type of the gasification process.

Nine candidate HGC processes were selected for the applicability assessments. These HGC processes and their active materials are the Air Products (CaO), Babcock and Wilcox (FeO), Battelle Northwest (molten salt mixture) CONOCO ($CaCO_3$), Foster Wheeler (Ni), IFP (ZnO), IGT-Meissner (molten Pb), Kennecott (Cu), and MERC (Fe_2O_3) processes. The selection was made to generate a large number of representative HGC processes each using a different type of active material in the absorbent. However, it was not intended to show a preference of one HGC process over another, where both use the same active material (e.g., MERC and IMMR processes both employ Fe_2O_3 as active material).

The H_2S removal efficiencies of the above HGC processes were estimated from thermodynamic equilibrium relationships for the respective absorbents, and compared with the minimum removal requirements presented in Table 14 to assess the applicability of each HGC process for the gasifier-end use pairs. Identical results were obtained for both the pressurized on-site combustion and combined cycle applications for the product gas characteristics as shown in Table 13. These results of these applicability assessments are presented in Table 15. It should be noted that for the applicability of the Battelle-Northwest process, the insufficient data are due to the uncertainties in the physical properties of the absorbent such as the temperature and pressure at which the carbonate mixture decomposes into solid oxides.

The applicability of HGC was then generalized to coals with different sulfur contents, by treating the hydrogen sulfide concentration in the fuel gas as a variable while keeping all the other parameters constant. The coal characteristics considered herein were assumed to be identical to those in Table 13, except for the variable sulfur content. As a point of reference for these assessments, the maximum H_2S concentrations in product gases that would not require any sulfur removal were estimated based on both the emission regulations and turbine specifications previously discussed. Table 16 shows the hydrogen sulfide concentrations below which no clean-up is required.

Applicability of the HGC processes for use in on-site combustion and combined cycle systems was then assessed between the H_2S concentration limits indicated in Tables 13 and 14 for the respective gasification options. For any H_2S product gas concentration in this range, the same result given in Table 15 was

TABLE 14 MINIMUM SULFUR REMOVAL FOR GASIFIER/END USE PAIRS*

Percent Sulfur Removal

End Use Gas from Gasifier	On-site Combustion	Combined Cycle	
	EPA's std.	EPA's std.	Turbine spec.
Lurgi (O_2)	80	57	71
Lurgi (Air)	80	19	67
Wellman-Galusha	85	20	74
MERC	80	29	75
BGC/Slagging	81	65	87
Winkler	83	64	93
Bi-Gas	81	4	70
Foster Wheeler (O_2)	79	60	83
Foster Wheeler (Air)	79	8	72

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* Based on product gas characteristics in Table 13

TABLE 15 - ASSESSMENT OF HGC PROCESS APPLICABILITY*

Gasifiers HGC Processes	Lurgi O_2/H_2O	Lurgi Air/H_2O	Wellman Galusha Air/H_2O	MERC Air/H_2O
Air Products	4	4	4	4
Babcock & Wilcox	4	1	1	1
Battelle Northwest	3	3	1	3
CONOCO	4	4	2	4
Foster Wheeler	1	1	1	1
IFP	4	1	1	1
IGT-Meissner	1	1	1	1
Kennecott	2	2	2	2
MERC	1	1	1	1

Explanation of numbering system:

1. Thermodynamically favorable, and gasifier product gas temperature is within range of HGC experimental test conditions.
2. Thermodynamically favorable, but gasifier product gas temperature is outside range of HGC experimental test conditions.
3. Insufficient data.
4. Unfavorable thermodynamics or absorbent properties.

* Results apply to both on-site combustion processes and combined cycles.

(continued)

TABLE 15 (continued)*

Gasifiers HGC Processes	BGC/Slagging O_2/H_2O	Winkler O_2/H_2O	Bi-Gas Air/H_2O	Foster Wheeler O_2/H_2O	Foster Wheeler Air/H_2O
Air Products	4	2	4	2	2
Babcock & Wilcox	1	4	4	4	4
Battelle Northwest	3	3	3	3	3
CONOCO	4	4	2	4	4
Foster Wheeler	2	4	4	4	4
IFP	1	4	4	4	4
IGT-Meissner	1	4	4	4	4
Kennecott	2	2	2	2	2
MERC	2	2	2	2	2

Explanation of numbering system:

1. Thermodynamically favorable and gasifier product gas temperature is within range of HGC experimental test conditions.
2. Thermodynamically favorable, but gasifier product gas temperature is outside range of HGC experimental test conditions.
3. Insufficient data.
4. Unfavorable thermodynamics or absorbent properties.

* Results apply to both on-site combustion processes and combined cycles.

TABLE 15 H_2S PRODUCT-GAS CONCENTRATIONS BELOW WHICH NO CLEAN-UP IS REQUIRED

End Use / Gasifier	H_2S concentration (wet mole %)	
	On-site Combustion	Combined Cycle
Lurgi (O_2)	0.12	0.18
Lurgi (Air)	0.11	0.18
Wellman Galusha	0.11	0.18
MERC	0.14	0.18
BGC/Slagging	0.30	0.18
Winkler	0.19	0.18
Bi-Gas	0.11	0.18
Foster Wheeler (O_2)	0.21	0.18
Foster Wheeler (Air)	0.14	0.18

obtained for both applications. This interesting result is due to a reduction in the H2S removal efficiency at decreasing concentrations of H_2S in the product gas.

Combining results presented in Tables 12 and 15, the applicability of the HGC processes for each selected gasifier-end use combination is obtained. These results are presented in Table 17. It should be noted that processes using Fe_2O_3 (such as MERC, IMMR) and Cu (such as Kennecott) are applicable for all gasifier-end use combinations under consideration.

TABLE 17 - HGC PROCESSES APPLICABLE FOR SELECTED GASIFIER-END USE COMBINATIONS

Gasifiers End Use	Lurgi (O_2)	Lurgi (Air)	Wellman-Galusha (Air)	MERC (Air)	BGC/Slagging (O_2)
On-site Combustion	Foster Wheeler* IGT-Meissner* Kennecott** MERC*	Babcock & Wilcox* Foster Wheeler* IFP* IGT-Meissner* Kennecott** MERC*	Babcock & Wilcox* Battelle Northwest* CONOCO** Foster Wheeler* IFP* IGT-Meissner* Kennecott** MERC*	Babcock & Wilcox* Foster Wheeler* IFP* IGT-Meissner* Kennecott* MERC**	Babcock & Wilcox* Foster Wheeler** IFP* IGT-Meissner* Kennecott** MERC**
Combined Cycle	Foster Wheeler* IGT-Meissner* Kennecott** MERC*	Babcock & Wilcox* Foster Wheeler* IFP* IGT-Meissner* Kennecott** MERC*		Babcock & Wilcox* Foster Wheeler* IFP* IGT-Meissner* Kennecott** MERC*	Babcock & Wilcox* Foster Wheeler** IFP* IGT-Meissner* Kennecott** MERC*

* Thermodynamically favorable, and gasifier product gas temperature is within range of HGC experimental test conditions.

**Thermodynamically favorable, but gasifier product gas temperature is outside range of HGC experimental test conditions.

(continued)

TABLE 17 (continued)

	Gasifiers			
End Use	Winkler (O_2)	Bi-Gas (Air)	Foster Wheeler (O_2)	Foster Wheeler (Air)
On-site Combustion	Air Products** Kennecott** MERC**	CONOCO** Kennecott** MERC**	Air Products** Kennecott** MERC**	Air Products** Kennecott** MERC**
Combined Cycle		CONOCO** Kennecott** MERC**	Air Products** Kennecott** MERC**	Air Products** Kennecott** MERC**

* Thermodynamically favorable, and gasifier product gas temperature is within range of HGC experimental test conditions.

** Thermodynamically favorable, but gasifier product gas temperature is outside range of HGC experimental test conditions.

SECTION 5

ADVANTAGES AND DISADVANTAGES OF HGC

The advantages and disadvantages of HGC are assessed generically relative to low temperature cleanup systems. Sections 5.1 through 5.5 present this comparison in terms of thermal efficiency, tars, particulates, NO_x, and corrosion. The uncertainties and problems of each particular HGC process are addressed in Section 3.

Economic comparisons between hot gas cleanup and low temperature desulfurization have been made by a number of investigators. The results of these studies are summarized in Section 5.6.

5.1 THERMAL EFFICIENCY

Cooling of the raw product gas for low temperature cleanup results in the condensation and removal of tars and the loss of the sensible heat of the gas. This reduces the overall thermal efficiency of the coal conversion processes used with low temperature cleanup, as compared to HGC processes.

In a recent study performed by Jones et al. (79) low and high temperature desulfurization processes are compared in terms of their thermal efficiencies. Two desulfurization processes (Benfield Process for low temperature desulfurization and MERC process for HGC) were coupled with five gasification options for combined cycle application. The process thermal efficiencies were then compared for gas turbine inlet temperatures of 1066°C (1950°F) amd 1316°C (2400°F). The results are given in Table 18.

As expected for all gasification options higher thermal efficiencies are obtained with HGC. The difference in thermal efficiency for the two cleanup options is greatest for Lurgi gasification. The reason is two-fold. First, Lurgi gasifiers produce tars, whose heating value is ultimately converted to electricity in a combined cycle application when HGC is used. When a low temperature desulfurization process is used, these tars are removed from the raw product gas by water scrubbing. In addition, Lurgi gasifiers require large amounts of steam to prevent clinckering of ash in the gasifier. This steam then appears in the raw product gas. When water scrubbing is employed, most of the sensible heat in the steam can not be used for steam generation. In the case of most other gasifiers, however, most of the steam fed to the gasifier is converted to hydrogen and carbon

TABLE 18

SUMMARY OF ESTIMATED THERMAL EFFICIENCIES (79)

Purification Process	Cold Benfield	HGC MERC	Cold Benfield	HGC MERC
Gas Turbine Inlet Temperature, ^{o}C	1066	1066	1316	1316
	Thermal Efficiency, %*			
Lurgi (O_2)	29.4	35.4	32.4	39.9
Lurgi (Air)	31.0	37.0	34.5	41.2
BGC Slagging (O_2)	36.5	37.5	39.6	40.6
Foster-Wheeler (O_2)	35.4	36.6	37.8	39.3
Foster-Wheeler (Air)	38.0	38.4	40.8	41.6

*Thermal Efficiency (%) $= \frac{(\text{Delivered kW})\ (3412.75)(100)}{(\text{Coal lb/h})\ (\text{Coal HHV Btu/lb})}$

monoxide in the gasifier. Thus, the associated efficiency loss due to the water scrubbing step is less than for the Lurgi gasifier.

The conversion of sulfur compounds from HGC regenerator to product sulfur also results in a loss of thermal energy. This loss in thermal efficiency is estimated to be 1.5 percent in the Jones study.

Ashworth, et al.(85) concluded that HGC should always yield greater power plant thermal efficiencies when compared with low temperature desulfurization. The incentive for HGC was found to be greater when tars are present in the fuel gas.

5.2 TARS

Tars consist of a mix of polycyclic and heterocyclic aromatic compounds produced from gasification of coal. The types of coal and gasification process affect the types and amounts of tars in raw product gases from coal gasifiers. For example, gasification of bituminous coals produces heavier tars than those generated from gasification of lignite. Also, the formation of heavier tars is favored at lower temperatures and pressures. The amounts of tars emitted from various types of gasifiers are discussed in Section 4.

If a low temperature cleanup process is used to purify a tar-laden gas, cooling of the gas stream in heat exchangers could cause condensation of tars at temperatures below 538°C (1000°F), resulting in fouling of the heat exchangers. As an alternative, water scrubbing can be used to remove the tars from the raw product gases upstream of any heat exchange or pollution control equipment. However, no environmentally acceptable method for treatment or disposal of tar-laden water stream has yet been demonstrated (40). In addition, the removal of tars implies a loss of some heating value (about 0.04-0.9 MJ/normal m^3 or 1-25 Btu/SCF) from the product gas resulting in reduced energy efficiency.

If desulfurization of tar-containing coal gases is carried out at temperatures above 538°C, then condensation of tars can theoretically be prevented. The tars would then pass through the absorber as vapors along with the product gas, and be combusted either in the boiler or the combustor of the gas turbine. Thus, the heating value of the tars would be conserved and utilized efficiently. If some tars should condense in cold spots of the hot gas desulfurizer, then they might cause operating problems such as a reduction in sorbent activity or plugging of the bed. If such tar deposition does not hinder the operation of the absorber, then the tars can be burned off in the regenerator (assuming that an oxygen containing gas is used for regeneration).

5.3 PARTICULATES

Gas streams from coal gasifiers contain particulates at various concentrations depending upon the type and operating conditions of the gasifier. These particulates are composed of carbon and mineral matter present in the coal. Sections 4.1.1 through 4.1.3 discuss particulate emissions from coal gasifiers.

The particulates may be objectionable because of environmental and/or process considerations. The New Source Performance Standard established by EPA for fossil fuel steam generators limits particulate emissions to 0.43 g/MJ (0.10 lb/106 Btu) heat input (83). For stationary gas turbines, no such standard has yet been established. However, in the case of gas turbines, particulates are objectionable because of process considerations, since they cause erosion and corrosion in the turbine. The erosion is due to the impact of the particulates on the turbine blades, while the corrosion results from the formation of sulfates and oxides, and the subsequent reaction of these compounds with the turbine metal. The particulate-related specifications for these turbines are based on engineering estimates, since gas turbines have not been commercially applied to coal gases. Westinghouse Electric Corporation projects a maximum allowance of 0.041 g/normal m^3 (0.018 gr/scf) for particle loading (at the turbine inlet), with no particles greater than 6 μm (74). For a typical particulate emission of 3.0 g/normal m^3 from a fixed bed gasifier - a minimum removal efficiency of 98.63 percent is required. For fluid and entrained bed gasifiers, the corresponding figures would be 26 and 110 g/m^3, and 99.84 and 99.96 percent removal efficiencies respectively.

The larger size particulates (i.e., $\geq$ 6 μm) from coal gasifiers can be efficiently removed by means of cyclones at temperatures up to 816°C (1500°F). If low temperature desulfurization is to be used, the effluent gas stream from the cyclones can then be cooled and water scrubbed to remove the smaller particulates Particulate free gas can then be directed to the sulfur removal equipment. If high temperature desulfurization is to be used, both the larger and smaller particles need to be removed at high temperatures.

The types of equipment that can be used to collect particulates include inertial separators, surface filters, scrubbers, granular bed filters, and electrostatic precipitators. The inertial separators (e.g., cyclones) do not remove fine particulate effectively. If such equipment were coupled with a HGC process that employes solid absorbents, then the particles from the gas stream would deposit on the HGC absorption bed and reduce the activity of the sorbent. If the HGC process uses a molten metal or salt absorbent, then the particulates would have to be separated from the molten absorbent. Such a separation might be very difficult.

Filters generally remove small particulates with a very high collection efficiency. Among them, the commercially available baghouse filters have not been used above 288°C (550°F). Ceramic fabrics and porous ceramic filters, on the other hand, can operate at temperatures up to 1650°C (3000°F), but are not commercially available (they are under development). Developmental work on a metallic filter by Brunswick Corporation has been discontinued (A-20).

Molten salt scrubbers can also be used at high temperatures. However, molten salt systems create additional problems, as discussed in Section 4. The major anticipated problems include corrosion caused by the molten salt, which necessitates the use of expensive construction materials, and the entrainment of salt particles in the gas stream from the scrubber.

Granular bed filters can remove small particulates with high collection efficiency, but have not been commercially used at high temperatures (above 430°C). Electrostatic precipitators have been tested at 1100°C, but have not been employed commercially above approximately 500°C.

It can be seen from the above discussion that no particulate control device is yet available to efficiently remove the particles from product gases of coal gasifiers.

5.4 NO_x

The combustion of a fuel gas produces nitrogen oxides such as NO, NO_2, and N_2O. These nitrogen oxides are usually referred as NO_x. The New Source Standard of Performance for coal-fired steam generators limits NO_x emissions (0.7 lb/10^6 Btu) to a maximum of 0.30 grams NO_x (expressed as NO_2) per megajoule of heat input. This standard does not apply to lignite-fired steam generators, for which the proposed limit is 0.60 lb $NO_x/10^6$ Btu heat input (83). For stationary gas turbines, the NO_x emission standard depends upon the heat rate (at peak load) of the gas turbine and/or the nitrogen content of the fuel.

NO_x emissions are generally in the range of 500-1000 ppm for coal-fired boilers, 100-1000 ppm for gas-fired boilers, and 100-500 ppm for oil-fired boilers (86). More than 90 percent of these emissions are in the form of NO, a relatively unreactive nitrogen oxide. For this reason, NO_x removal is a difficult problem, and the most effective method of control is to limit its formation during the combustion process.

The sources of nitrogen in a coal derived fuel gas consist of the atmospheric nitrogen and the nitrogen in the coal. The NO_x emissions due to the atmospheric nitrogen can be controlled by the design and operating conditions, flame temperature, excess air, and residence time in the combustor. The gasification of coal also produces nitrogen compounds primarily in the form of ammonia and some hydrogen cyanide and pyridene. The concentrations of these nitrogen compounds in the fuel gas vary with the gasifier operating conditions, with lower temperatures and higher pressures favoring the formation of such nitrogen compounds. These nitrogen compounds are readily combustible to product NO_x.

When low temperature desulfurization is used, the fuel gas from the gasifier is scrubbed with water. This scrubbing process removes the ammonia and other nitrogen compounds, and, therefore, results in reduced NO_x emissions. On the other hand, when HGC is used, the raw gas from the gasifier is first introduced to the particulate removal equipment and then to the high temperature desulfurization unit. Thus, the nitrogen compounds are not removed and, therefore, contribute to the NO_x emissions from combustion in the boiler or turbine.

Decompostion of ammonia into stable nitrogen and hydrogen may be a solution to the above NO_x emission problem (57). The decomposition reaction is as follows:

$$NH_3 \rightleftharpoons 1/2\ N_2 + 3/2\ H_2$$

The decomposition of ammonia is thermodynamically favored at high temperatures and low pressures. The effect of pressure is very small, increasing the partial pressure equilibrium constant (K_p) by 3 percent for a reduction in pressure from 30 to 10 atmospheres (temperature range 349-399°C. On the other hand, K_p is strongly dependent upon temperature; its value being 38 at 349°C (660°F), 76 at 399°C (750°F) and 152 at 449°C (840°F), all at 10^6 Pa (10 atm) pressure. However, the kinetics for reaction are slow and a catalyst is needed to speed the rate of this reaction. This problem of converting NO_x to ammonia and then decomposing the latter via a catalyst has already been addressed by the automobile manufacturing companies, such as General Motors(87) and Ford Motor Company (88). Various developed catalysts containing Ni, Pt, W, Mo and Ru all have the deficiency of getting poisoned with sulfur compounds remaining in the gas after the cleanup. Another problem associated with the use of these catalysts is sintering, which would result in reduced activity. The only commerical catalysts reported in the literature that is potentially capable of decomposing ammonia contains 5 percent Fe_2O_3 in inert alumina. Since this catalyst contains the same active material as some HGC processes (such as MERC and IMMR processes), it might be possible to combine HGC and NH_3 removal into one step. Further research is needed to determine the feasibility of such an operation.

5.5 CORROSION

Certain chemical compounds that originate from coal or the absorbent material can cause corrosion of the equipment. Corrosion problems appear to be much more severe for HGC than low temperature desulfurization processes.

In the low temperature processes, corrosion may take place during the cooling of the raw product gas and the treatment of the liquid stream. During the cooling of the raw product gas, condensation and deposition of KCl and NaCl as solid particles on the waste heat boiler tubes may cause corrosion. Iron base alloys experience oxidation at temperatures above 482°C (300°F), and nickel base alloys above 649°C (1200°F). Corrosion by the condensates has been observed in gas cleanup systems used in by-product coke oven installations and in Koppers systems (89).

In the case of HGC processes, various process equipment is exposed to corrosion with H_2S at high temperatures. Tests conducted by the Westinghouse Research Laboratory (89) at 1000°C (1832°F) showed that Incoloy 800, aluminized Incoloy 800 and L605 (a cobalt-based superalloy) are more corrosion resistant than other metals. However, none of these materials was found to be satisfactory at an H_2S concentration of 0.5 mole percent. Corrosion tests, performed by IMMR on six metal specimens (1020 C.S., 304 S.S., 316 S.S., Incoloy 600, Inconel 800 and Armco 18) at 649°C (1200°F) with a gas containing 1 percent H_2S and 3 percent H_2O showed that Armco 18 withstood attack best, and that metals with low nickel content and chromium to nickel ratios above 0.5 were most corrosion resistant (28). More information on the H_2S corrosion problem is presented in Section 3.

In addition to H_2S, alkali metals can also cause corrosion. These alkali metals orginate from coal, water, and sometimes the absorbent material. Dolomites contain sodium and potassium. The absorbents in the three molten salt processes described in Section 3 also contain these alkalis. Upon combustion of the fuel gas, alkali metal sulfides convert to sulfates, and then condense on the turbine blades (if the end use is combined-cycle), which results in corrosion and failure of the turbine blades. Similarly, alkali chlorides from the fuel gas may condense and cause corrosion. Information on corrosion problems due to molten salt absorbents can be found in Section 3.

5.6 ECONOMIC ANALYSIS

A comparative economic analysis of HGC versus low temperature desulfurization processes was performed by various investigators.

A study by Robson, et al,(82,90) compares HGC with low temperature desulfurization of coal gases from the Bi-Gas gasifier for the combined cycle application. The Selexol Process was selected for low temperature cleanup, whereas the CONOCO Process was chosen for HGC. This study shows that the overall thermal efficiency improves with HGC (45.0 percent for HGC versus 43.5 percent for low temperature clean-up), and that the costs of generating electricity are 24.2 mill/kWh with HGC and 25.4 mills/kWh with low temperature cleanup.

In a more recent study by Jones, et al, (79) coal gasification-combined cycle power plants of 1,000 MW capacity were considered for two possible values of gas turbine inlet temperatures (1066°C and 1316°C). The MERC Process was chosen as the representative of HGC processes, since it was judged to be at a more advanced stage than the CONOCO, Air Products or Battelle Northwest Processes. The Benfield Process was chosen as the representative of low temperature desulfurization processes. Five gasification options were considered, including the air blown Lurgi (fixed bed), oxygen blown Lurgi (fixed bed), oxygen blown BGC (slagging, fixed bed), and air blown Foster Wheeler (entrained bed) gasification processes.

In the combined cycle power plant designs with HGC, the raw product gas from the gasifier passes through the particulate removal equipment and the MERC H_2S absorber, and is then combusted before being expanded in the gas turbine. Sulfur dioxide in the MERC regenerator effluent gas is converted to sulfur with the Applied Chemical SO_2 reduction technology, which uses the fuel gas as the reducing agent (79).

In the combined-cycle power plant designs with low temperature desulfurization, the raw product gas from the gasifier is quenched with water, desulfurized in the Benfield Plant, and then introduced into the combustor of the gas turbine. The liquid stream from the quench operation is treated, and tars are separated. The gas stream from the Benfield Plant is treated in a Claus Plant and tail gas incinerator (79).

The economic assumptions used by Jones, et al (79), can be summarized as follows:

- Mid-1975 dollars with no escalation,
- 36 - month construction period,
- 10 percent construction loan interest, compounded quarterly,
- Coal cost of \$1.00/MM Btu (Illinois # 6, HHV: 12,235 Btu/lb as received),
- 70 percent operating load factor,
- 25 - year plant life,
- 50:50 debt to equity ratio,
- Eight percent bond interest, compounded semiannually,
- 12 percent return on equity after taxes, compounded semiannually, and
- 15 percent contingency in plant investment costs.

The estimated capital requirements and costs of electricity for coal gasification-combined cycle power plants are presented in Table 19 and 20. Table 21 summarizes the estimated capital requirements for the purification system components (79).

Tables 19 and 20 show that there is a considerable incentive in cleaning the Lurgi gas at high temperatures. The reductions in costs for HGC are 34 percent for capital requirements and 30 percent for the cost of electricity. However, the incentive for using HGC for the other types of gasification options is relatively small.

The attractiveness of HGC for Lurgi gasification is due to the presence of large amounts of steam and tars in the gasifier effluent gas. Low temperature desulfurization of the Lurgi gas requires a large water treatment facility and a tar-fired boiler with stack gas scrubber, which would result in a substantial increase in costs. For the other gasification systems, such a large increase does not occur due to the small amount of steam and the absence of tars in the raw product gases.

TABLE 19

SUMMARY OF ESTIMATED CAPITAL REQUIREMENTS FOR 1,000 MW GASIFICATION - COMBINED CYCLE POWER PLANTS (79)

Capital Requirements \$/kW*

	Gas Turbine Inlet Temp. 1066°C		Gas Turbine Inlet Temp. 1316°C	
Gasification Process / Purification Process	Cold Benfield	HGC MERC	Cold Benfield	HGC MERC
Lurgi (O_2, Dry Ash)	1,117	739	1.046	703
Lurgi (Air, Dry Ash)	1.000	667	936	642
BGC Slagging (O_2)	643	629	629	606
Foster Wheeler (Air)	619	616	604	597
Foster Wheeler (O_2)	670	679	658	657

* Capital Requirements (\$/kW) correspond to Plant Investment with adjustments for Illinois Sales Tax, Preproduction Costs, Royalty Payments, Initial Catalyst and Chemicals, Construction Loan Interest and Working Capital.
The Capital Requirements tabulated above represent an increase of 34 percent over the Plant Investment estimates due to inclusion of these allowances.

TABLE 20

SUMMARY OF ESTIMATED COSTS OF ELECTRICITY FOR GASIFICATION-COMBINED CYCLE POWER PLANTS OF 1,000 MW CAPACITY (79)

Power Costs, Mills/kWh*

	Gas Turbine Inlet Temp. 1066°C		Gas Turbine Inlet Temp. 1316°C	
Gasification Process / Purification Process	Cold Benfield	HGC MERC	Cold Benfield	HGC MERC
Lurgi (O_2)	48.3 (60.2)**	33.8 (43.7)	44.9 (55.5)	31.6 (40.4)
Lurgi (Air)	43.8 (55.0)	31.1 (40.5)	40.6 (50.7)	29.3 (37.7)
BGC Slagging (O_2)	30.4 (39.9)	29.7 (39.0)	29.2 (38.0)	28.2 (36.8)
Foster Wheeler (Air)	29.2 (38.4)	29.0 (38.1)	28.1 (36.7)	27.7 (36.1)
Foster Wheeler (O_2)	31.5 (41.4)	31.5 (41.1)	30.5 (39.8)	30.2 (39.1)

* Based on: Delivered coal costs of $1.00/MMBtu. Mid-1975 dollars with no escalation included and an operating load factor of 70 percent.

** Numbers in parentheses represent Power Costs related to a delivered coal cost of $2.00/MM Btu.

TABLE 21

SUMMARY OF ESTIMATED CAPITAL REQUIREMENTS FOR THE PURIFICATION SYSTEM COMPONENTS OF EACH CONFIGURATION INVESTIGATED (79)

Capital Requirements $/kw*

	Gas Turbine Inlet Temp. 1066°C		Gas Turbine Inlet Temp. 1316°C	
Gasification Process / Purification Process	Cold Benfield**	HGC MERC***	Cold Benfield**	HGC MERC***
Lurgi (O_2)	141	115	129	103
Lurgi (Air)	126	121	114	109
BGC Slagging (O_2)	52	87	48	80
Foster Wheeler (Air)	102	106	95	99
Foster Wheeler (O_2)	86	99	80	93

* Based on mid-1975 dollars with no escalation included.

**Cold purification costs include the costs of the H_2S scrubbing system, the Claus plant, the tail gas treating system as well as crude gas cooling equipment.

***Hot purification costs include the costs of the iron oxide system, the SO_2 recycle and sulfur recovery systems, and the high temperature particulate removal devices upstream and downstream of the iron oxide system.

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APPENDIX A

PERSONAL COMMUNICATIONS

A-1. Robert Rieve, Atlantic Richfield Corporation, December, 1978.

A-2. A.M. Squires, Virginia Polytechnic Institute, January, 1978.

A-3. R. Pfeffer, City College of New York, December, 1978.

A-4. Edward Nemith, Bureau of Research, U.S. Steel Corporation, Pittsburh, Pennsylvania, April, 1978.

A-5. R. K. Bhada, Babcock & Wilcox Co., January, 1978.

A-6. H.P. Markant, University of Kentucky (formerly with Babcock & Wilcox), January, 1978.

A-7. Joseph Oxley, Battelle Columbus Laboratories, April, 1978.

A-8. J.T. Schrodt, University of Kentucky, August, 1978.

A-9. J.C. Agarwal, Kennecott Copper Corporation, Ledgement Laboratory, January, 1978.

A-10. J.R. Sinek, Kennecott Copper Corporation, Ledgement Laboratory, January, 1978.

A-11. W. R. Gutmann, Catalysts and Chemicals, Inc., December, 1978.

A-12. A. Deschamps, Institute Français du Pétrole, August, 1978.

A-13. K.S. Wheelock, Exxon Research and Engineering Co., April, 1978.

A-14. Peter Steiner, Foster Wheeler Energy Corporation, April, 1978.

A-15. Carl Gutterman, Foster Wheeler Energy Corporation, May, 1978.

A-16. Raymond Moore, Battelle Pacific Northwest Laboratories, December, 1978.

A-17. Wen Soung, Hydrocarbon Research, Inc. Trenton, New Jersey, December, 1977.

APPENDIX (cont'd)

A-18. Dennis Duncan, Institute of Gas Technology, Chicago, Illinois, January, 1978.

A-19. Douglas Bell, U.S. Environmental Protection Agency, IERL-RTP, N.C., December, 1978.

A-20. K. Mills, Brunswick Corporation, August, 1978.